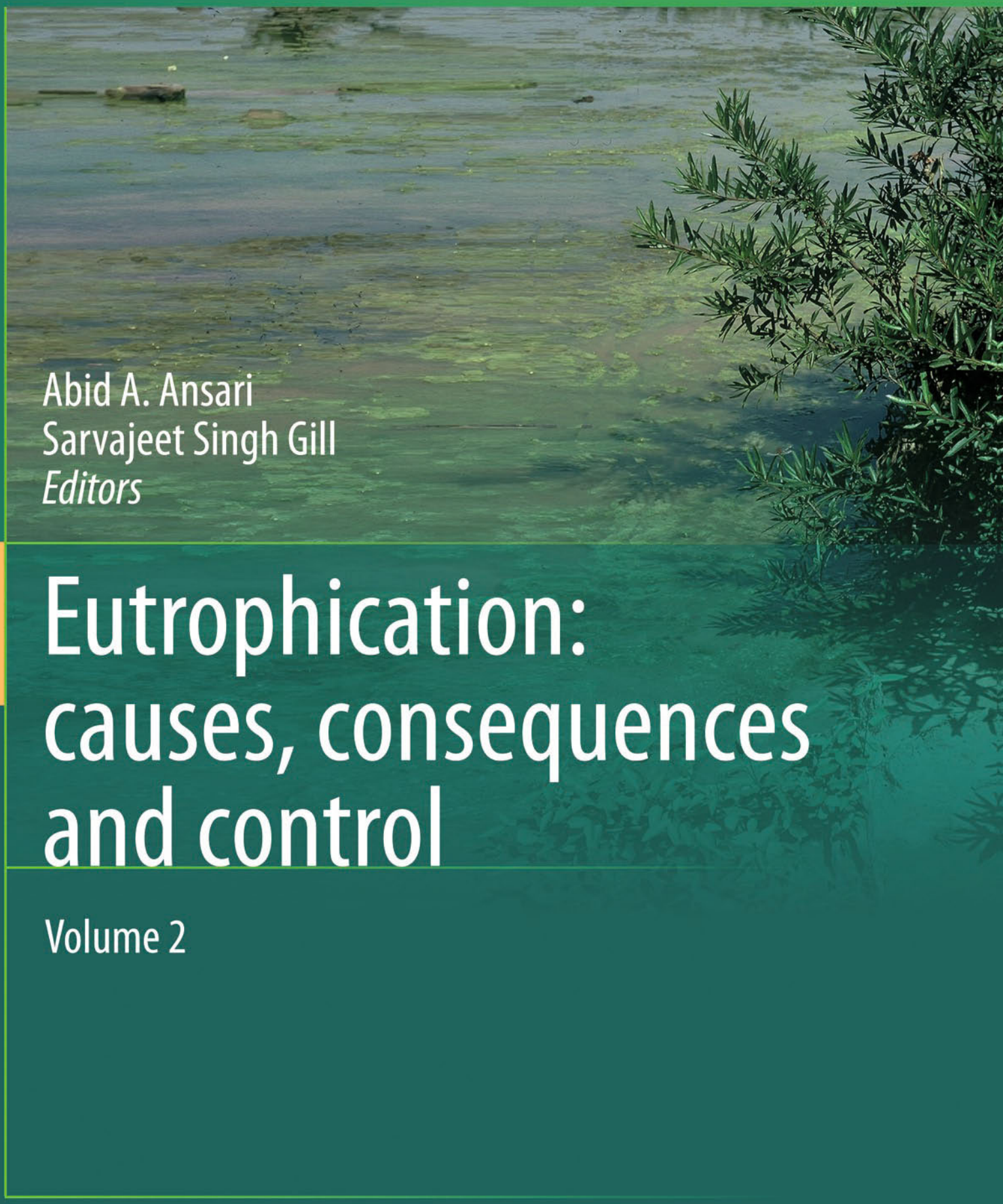

Abid A. Ansari
Sarvajeet Singh Gill
Editors

Eutrophication: causes, consequences and control

Volume 2

Springer

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Abid A. Ansari • Sarvajeet Singh Gill
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Preface

> Anyone who can solve the problems of water will be worthy of two Nobel Prizes—one for Peace and one for Science
>
> John F. Kennedy

Water is an indispensable resource and essential life supporting factor. On the hydrological map of the world, eutrophication is one of the great issues causing degradation of these freshwater ecosystems. The excessive nutrient enrichment of waters results in change of oligotrophic water bodies to mesotrophic, eutrophic and finally to hypertrophic. The major nutrient sources for enrichment of aquatic ecosystems are sewage, household detergents, industrial discharges, runoff from agriculture, construction sites, and urban areas. Eutrophication is a threat for water used in fisheries, recreation, industry, and drinking as it causes the increased growth of cyanobacteria and aquatic macrophytes resulting in low oxygen, death, and decomposition of aquatic flora and fauna. Thousands of lakes and reservoir estuaries and wetland around the globe near the large population centers has been deteriorating due to rising nutrient levels and other chemical pollutants causing changes in their ecological structure and function. Eutrophication can be minimized by reducing nutrient use in fertilizers and household detergents. The economic analysis is urgently required and devising some policies to make desired changes in agricultural practices is needed to control the eutrophication. The improved soil management practices, treatments of water, mathematical models, and bioremediation are some of the effective tools to combat eutrophication in aquatic ecosystems. The public awareness and education on eutrophication also play an important role in preventing the eutrophication of water bodies.

The consequence of man-made eutrophication of freshwaters is severe deterioration of water quality which is now a big matter of interest for the scientific community. The research in this field has suddenly increased in last few years and many books, research papers, reviews, and articles which dealt with eutrophication and related management issues have been published so far. In this series of publications, we have taken the task to publish the second volume of the book "Eutrophication: Causes, Consequences and Control" after the successful publication of its first volume in 2011. Eutrophication: Causes, Consequences and Control Volume-II covers a collection of 18 chapters written by 44 experts. The book presents the latest literature and research findings on eutrophication. The chapters from this book provide complete information on the topic of eutrophication and its related areas. It can be a resourceful guide suited for scholars and researchers. Chapter 1 will give general information including definitions, drivers, environmental conditions, and the control measures of eutrophication. Chapter 2 highlights the changes in the delicate balance between seasonal, spatial, and littoral dynamics, and the resulting biogeochemical changes in the eutrophic water bodies. Chapter 3 deals with impacts of eutrophication on the structure and functioning of aquatic ecosystem. Chapter 4 focuses on the economics related to eutrophication and its control measures. Chapter 5 covers the cultural eutrophication in lakes leading to the degradation of water quality and depletion of aquatic biodiversity. Chapter 6 deals with the structure and components of the food webs and trophic links between them in eutrophic lakes.

Chapter 7 focuses on anthropogenic perturbations on freshwater ecosystems as a consequence of tourism. The lakes, ponds, and other freshwater reservoirs are the places of attraction for the public which causes touristic impacts on the reservoirs especially in terms of

eutrophication. Chapter 8 gives information about the eutrophication in the Great Lakes of the Chinese Pacific Drainage Basin. The changes, trends, and management strategies are elaborated in this chapter. Chapter 9 discusses the changes in photoautotrophic productivity of lakes, reservoirs, rivers, and streams under the direct threat of eutrophication. Chapter 10 deals with nutrient dynamics in the inner Saronikos gulf and the changes occurred over the last 25 years due to the sewage discharges releasing from the Sewage Treatment Plant of Athens in Psittalia Island. The environmental status of the inner Saronikos gulf is also presented in this chapter. Chapter 11 sheds light on eutrophication and its associated changes in salt marshes which have an important role in biogeochemical cycles. Chapter 12 covers research work to evaluate the role of phosphate-containing household detergents in the eutrophication and deterioration of fresh water ecosystems.

Chapter 13 deals with the hypothesis of the trophic cascade relations especially between fish trophic guilds, limnology, and application of morphoedaphic index studied in the Itaipu Reservoir (Brazil). Chapter 14 describes the eutrophication status in seven coastal estuaries of southeast Australia where phytoplankton species diversity and their ecological characteristics were found as strong indicators of eutrophication. Chapter 15 deals with the biogeochemical indicators of eutrophication in wetlands. Chapter 16 deals with role of mineral nutrients in eutrophication. Chapter 17 is about the development of sustainable phytoremediation systems and the most suitable environmental conditions to recover the nutrients from eutrophic waters. Chapter 18 covers the eutrophication studies on King Abdullal Canal in Jordan Valley, Mujib dam, Wadi Rajil dam in the eastern desert of Jordan, and Muwaqqar dams in the eastern highlands of Jordan. The study reveals the significant role of ultraviolet radiation and bromide as limiting factors of eutrophication processes in the context of semiarid climate zones. The editors and contributing authors hope that this book will update the knowledge of eutrophication and its related fields on a global scale. This book will lead to new researches, methodologies, discussions, and efforts to overcome this global problem of eutrophication with minimum economic loss.

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Abid A. Ansari
Sarvajeet S. Gill

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Eutrophication: Challenges and Solutions

1

M. Nasir Khan and F. Mohammad

Abstract

On the hydrological map of the world eutrophication has become the primary water quality issue. The excessive enrichment of waters with anthropogenic sources of nutrients especially nitrogen (N) and phosphorus (P) lead to the transformation of oligotrophic water bodies to mesotrophic, eutrophic, and finally hypertrophic. Mesotrophic and eutrophic phases exhibit intermediate and rich levels of nutrients and show increasing and serious water quality problems, respectively. Eutrophication restricts water use for fisheries, recreation, industry, and drinking because of increased growth of undesirable algae and aquatic weeds and the oxygen shortages caused by their death and decomposition. Associated periodic surface blooms of cyanobacteria (blue-green algae) occur in drinking water supplies and may pose a serious health hazard to animals and humans. Anthropogenic activities are the worst culprit of nutrient enrichment and root cause of eutrophication of water bodies. Excess nutrient inputs to water bodies usually come from sewage, industrial discharges, agricultural runoff, construction sites, and urban areas. Eutrophication can be minimized by regulating the nutrient sources, reducing the use of fertilizers, proper soil management practices, implementing mathematical models, phytoremediation etc. Among these, public awareness of eutrophication can play an important role in preventing the eutrophication of water bodies.

Keywords

Eutrophication · Fertilizers · Livestock intensification · Nitrogen · Phosphorus · Phytoremediation · Wastewater flow

1.1 Introduction

During the early stages of formation, water bodies are in the state of *oligotrophy* and support a pitiful of aquatic life because of nutrient deficiency. Enrichment of water with mineral nutrients, such as nitrogen (N) and phosphorus (P) causes transformation of water bodies from oligotrophic to mesotrophic, eutrophic, and finally hypertrophic stage (Fig. 1.1). Mesotrophic and eutrophic phases exhibit intermediate and rich levels of nutrients and show increasing and serious water quality problems, respectively. Whereas, hypertrophic phase is the excessive enrichment of aquatic and terrestrial ecosystem with anthropogenic sources of nutrients is termed as *eutrophication* which has been identified as the main cause of impaired surface water quality. Eutrophication restricts water use for fisheries, recreation, industry, and drinking because of increased growth of undesirable algae and aquatic weeds and the oxygen shortages caused by their death and decomposition. Associated periodic surface blooms of cyanobacteria (blue-green algae) occur in drinking water supplies and may pose a serious health hazard to animals and humans (Fig. 1.1).

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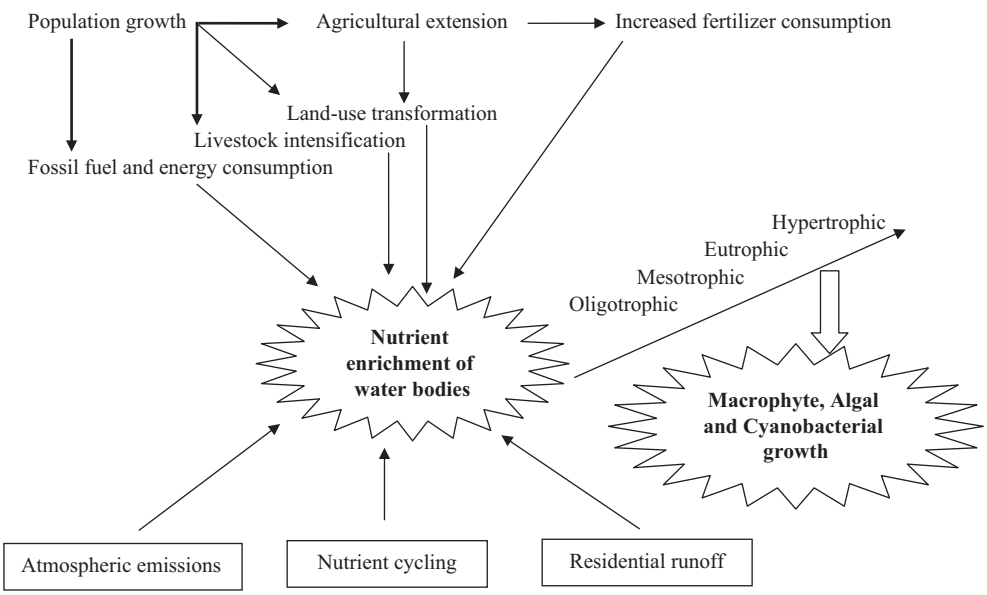

Fig. 1.1 Simplified illustration of eutrophication driven by synergistic action of direct and indirect drivers

Eutrophication of water bodies is occurs due to overenrichment by nutrients, principally phosphorus (Schindler 1977), followed by uncontrolled growth of primary producers and episodes of oxygen depletion owing to decomposition of algal organic matter. Excess phosphorus inputs to water bodies usually come from two types of nutrient sources, point sources such as sewage, industrial discharges, and nonpoint sources such as runoff from agriculture, construction sites, and urban areas. Nonpoint sources of nutrients have replaced point sources as the driver of eutrophication in many regions (Carpenter et al. 1998). An important driver of nonpoint nutrient input is excessive application of fertilizer or manure, which causes phosphorus to accumulate in soils (Bennett et al. 2001). Phosphorus-rich soils are washed into lakes, where some of the phosphorus dissolves and stimulates growth of phytoplankton and aquatic plants.

Prevailing eutrophication by anthropogenic nutrient inputs is a relatively recent environmental problem. Intensive fertilization of agricultural soils and associated nonpoint inputs of phosphorus increased through the middle of the twentieth century (Carpenter et al. 1998; Bennett et al. 2001). It could take 1,000 years or more to recover from eutrophication caused by agricultural overenrichment of soils (Carpenter 2005).

1.2 Causes of Eutrophication

There are a number of sources of nutrients causing eutrophication of water bodies. All activities in the entire drainage area of a lake or reservoir are reflected directly or indirectly in the water quality of water bodies. A lake or reservoir may, however, be naturally eutrophied when situated in a fertile area with naturally nutrient-enriched soils. In many lakes and reservoirs wastewater is the main source since untreated wastewater or wastewater treated only by a conventional mechanical–biological methods still contains nitrogen (25–40 mg/l) and phosphorus (6–10 mg/l). In fact, agriculture (including livestock agriculture) is the largest source of nonpoint water pollution. Drainage water from agricultural land contains phosphorus and nitrogen. It usually has much more nitrogen because phosphorus is usually bound to soil components. Extensive use of fertilizers results in significant concentrations of nutrients, particularly nitrogen, in agricultural runoff. If eroded soil reaches the water bodies, both phosphorus and the nitrogen in the soil contribute to eutrophication. Erosion is often caused by deforestation which also results from unwise planning and management of the resource.

Nitrates, because of their water-soluble nature, move readily with surface runoff into rivers or with water percolating through the soil profile into the groundwater below. A 1998 assessment of nonpoint sources of N and P to waters in the USA (conducted by the Ecological Society of America) determined that only about 18% of the nitrogen that is applied to fields as fertilizers leaves the fields in the form of produce and the remaining 82% is left behind as residue or in soils, where it either accumulates, erodes with the soil (often to surface waters), leaches to groundwater, or volatilizes into the atmosphere.

Unlike nitrate, however, phosphate is not water soluble, so it moves only with soil movement as it adheres to soil particles. When it erodes on soils from agricultural fields, it is essentially nonrecoverable, washing into sediments in oceans. The global P budget concludes that P is accumulating in the world's soils (that is, inputs, largely from fertilizers, animal feeds, and animal wastes, are greater than removals in harvested crops and meat). The result of this imbalance

between input and output is that the net P storage in soil and fresh water ecosystems of the world is estimated to be about 75% higher than during preindustrial times. A large portion of this P accumulation is in agricultural soils, as might be expected. A major problem associated with this increased P content of soils is that any factors that increase soil erosion will also increase runoff of P with soil to streams, rivers, lakes, and coastal regions.

Nutrients entering waterways come from a variety of sources and originate from two main categories, direct and indirect sources.

1.3 Drivers of Eutrophication

Drivers of the ecosystem often interact with one another in synergistic ways in causing increased occurrence of eutrophication. Direct drivers of eutrophication include higher energy consumption, increased fertilizer consumption, land-use change etc. Population growth, economic growth, structural change, and globalization are the most commonly identified indirect drivers that impact consumer consumption and the growth of intensive agriculture.

1.3.1 Direct Drivers of Eutrophication

Direct drivers are usually associated with intensive agriculture and discharges at a particular point. These include piggeries, sheep holding yards, dairies and horticulture, meat processing plants, vegetable processing plants, fertilizer factories, and other industries. Intensive animal industries often produce large quantities of wastewater and nutrients. Nutrient concentrations in these wastes are often much higher than those leaving indirect sources. Many of these industries currently combine ponding, irrigation, and diversion to waterways to dispose of nutrient-rich wastewater. Humans discharge the equivalent of 1 kg of phosphorus annually as a result of domestic activities. Detergents make up approximately 50%. Disposal in septic tanks or improperly constructed or sited sewerage works can lead to nutrient contamination of both ground and surface waters.

1.3.1.1 Wastewater Flow

Municipal wastewater treatment plants and industrial wastewater discharges, nitrogen leaching from below-ground septic tanks, and storm water runoff are some of the urban and industrial sources of nutrient losses. They are typically the most controllable sources of nutrients and are often regulated in developed countries. The most prevalent urban source of nutrient pollution is human sewage, although its importance varies by region and country. Sewage is estimated to contribute 12% of riverine nitrogen input in the USA, 25% in Western Europe, 33% in China, and 68% in the Republic of Korea (MA 2005). Urban wastes are processed in sewage treatment plants that work on the principle of bacterial oxidation of organic matter. In this way, all the major elements from the wastes are oxidized. These elements therefore become soluble and drain in high concentration in the effluent from the treatment plant. Such effluents are point sources of nitrogen and phosphorus.

Storm water runoff is another significant source of nutrients from urban areas. Rainfall events flush nutrients from residential lawns and impervious surfaces into nearby rivers and streams. In some cities, combined sewer overflow (CSO) systems worsen storm water runoff problems. CSOs are designed to collect rainwater, domestic wastewater, and industrial wastewater in the same pipe. During heavy rain or snowmelt, wastewater volume can exceed the capacity of the CSO system, as well as that of the wastewater treatment plant receiving the flow. As a result, the excess wastewater, including raw sewage, is discharged directly into nearby streams and rivers.

For industrial sources of nutrient pollution, certain industries are larger sources than others. Pulp and paper mills, food and meat processing, agroindustries, and direct discharge of sewage are some of the larger sources of industrial nutrient pollution. Industrial wastes and domestic sewage together are the major urban sources of nutrient overload, responsible for 50% of the total amount of phosphorus unloaded into lakes from human settlements (Smith et al. 2006). Approximately 15% of the US population contributes phosphorus-containing wastewater effluents to lakes, resulting in eutrophication (Hammer 1986). By 1970, nearly 10,000 public lakes had been affected by excessive human-influenced nutrient enrichment (Knud-Hansen 1994).

1.3.1.2 Livestock Intensification

The rapidly changing nature of raising livestock has also contributed to a sharp increase in nutrient fluxes over the last century. Animal production is intensifying with increasingly more production occurring further away from feedstock supplies. The large quantity of manure produced by these operations is applied to land as fertilizer, stacked in the feedlot, or stored in lagoons. The consequence is that livestock units become point sources of nutrients runoff rather than diffuse sources, and under improper management practices they may pose serious problems. They may contribute to organic pollution of the receiving body of water as well as nutrient enrichment. Frequently, the rate and timing of land application of manure is dictated by the volume and availability of manure and not by crop needs. This leads to ill-timed application or overapplication of manure, further exacerbating nutrient runoff and leaching.

In China, meat production rose by 127% between 1990 and 2002 (FAO 2009), but fewer than 10% of an estimated 14,000 intensive livestock operations have installed pollution controls (Ellis 2007). In the Black Sea region, one swine operation, which subsequently closed, had over 1 million pigs and generated sewage equivalent to a town of 5 million people (Mee 2006).

Aquaculture is one of the growing sources of nutrient pollution. Annual aquaculture production worldwide increased by 600%, from 8 million tons in 1985 to 48.2 million tons in 2005. Nearly 43% of all aquaculture production is within marine or brackish environments, with the remainder in freshwater lakes, streams, and man-made ponds (FAO 2007). Marine fish and shrimp farming generate concentrated amounts of nitrogen and phosphorus from excrement, uneaten food, and other organic waste. If improperly managed, aquaculture operations can have severe impacts on aquatic ecosystems as nutrient wastes are discharged directly into the surrounding waters. For every ton of fish, aquaculture operations produce between 42 and 66 kg of nitrogen waste and between 7.2 and 10.5 kg of phosphorus waste (Strain and Hargrave 2005).

1.3.1.3 Fossil Fuel and Energy Consumption

Coal-fired power plants, cars, buses, and trucks consume fossil fuels, which is also a contributor of nutrients. On combustion fossil fuel releases nitrogen oxides into the atmosphere. These oxides of nitrogen contribute to the formation of smog and acid rain. Nitrogen oxide is redeposited to land and water through rain and snow, or can settle out of the air in a process called dry deposition. Fossil fuel combustion contributes approximately 22 Tg of nitrogen pollution globally every year, approximately one-fifth of the contribution of synthetic nitrogen fertilizers (MA 2005). In the Baltic Sea, atmospheric deposition, primarily from burning fossil fuels, accounts for 25% of nitrogen inputs (HELCOM 2005). Similarly, in the Chesapeake Bay, atmospheric deposition accounts for 30% of all nitrogen inputs. In some areas, such as in the US North Atlantic, atmospheric deposition of nitrogen can exceed riverine nitrogen inputs to coastal areas (Spokes and Jickells 2005).

Increasing demand of energy for the increasing population across the globe is one of the direct drivers of eutrophication. Total worldwide energy consumption rose by 33% between 1990 and 2005. Currently, more than 86% of the world's energy needs are being met by fossil fuel sources (EIA 2008). Experts estimate that per capita energy consumption will increase by approximately 18% between 2005 and 2030, while total global energy consumption will rise by 50%; the developing world is projected to account for the majority of increased energy consumption (EIA 2008). Fossil fuels are expected to continue meeting approximately 86% of global energy needs (EIA 2008).

1.3.1.4 Increased Fertilizer Consumption

The increasing population forces to increase the agriculture production that is accompanied by the additional use of fertilizers. It is expected that between 2002 and 2030 fertilizers consumption will increase by 40% (FAO 2000). The majority of the projected increase in global fertilizer consumption is attributed to the developing world where food production and adoption of intensive agricultural practices are expected to increase (FAO 2000). At present, two sources of fertilization commonly used are slurry and synthetic compounds. Nitrogen and phosphorus losses in surface runoff from fertilized soils depend upon the quantity of transporting water and the time and rate of fertilizer application. When fertilizers are applied before a wet period or snowmelt, or on frozen ground, losses are higher than when fertilization is done in the spring. Excessive application of fertilizers and bad management practices increase nutrient loss from the soil. Lesser amounts of nitrogen and phosphorus are lost to the surface water of judiciously fertilized and well-managed soils.

1.3.1.5 Land-use Transformation

Enhanced food production is coupled with the transformation of forest to crop land. Cropland has experienced a net global increase of about 3 million ha per year from 1995 to 2002, with over 90% of the total cropland gains coming from forests (Holmgren 2006). Agriculture is also the single largest cause of wetland loss. Approximately 50% of the world's wetlands have been lost since the 1950s. The majority of wetland loss occurred as a result of drainage for agricultural production (OECD/IUCN 1996). According to the prediction of FAO, land-use conversion for agriculture will continue, but at a slower pace than in the past (FAO 2002). Natural landscapes such as forests and wetlands are important for capturing and cycling nutrients. Increasing land-use conversion reduces the ability of these landscapes to intercept nutrients and leads to greater nutrient losses to local waterways.

1.3.2 Indirect Drivers of Eutrophication

1.3.2.1 Population Expansion

Although population growth is an indirect driver of eutrophication but it is also the root cause for all types of the drivers of eutrophication. The global population is predicted to grow from 6.5 billion in 2005 to nearly 9.2 billion in 2050 with the majority of population growth occurring in developing countries (United Nations Population Division 2008). Population growth will increase the demand for food, land, energy, and other natural resources, ultimately leading to greater agricultural production and increased burning of fossil fuels to heat homes, power cars, and fuel industry.

1.3.2.2 Financial Boom

Increasing economic growth and per capita income indirectly contributes the nutrient pollution in developing parts of the world. Increasing incomes will lead to changes in dietary choices, increasing energy use, and increasing consumption of consumer goods. Worldwide increase in purchasing power is moving dietary trends toward greater meat consumption especially in the case of lower to middle income populations (FAO 2002). The increased livestock production that will be necessary to meet growing global demand for meat is expected to have significant implications for the severity of nutrient pollution worldwide. It is estimated that only 20 % of the nitrogen used in swine production is actually consumed by humans, the remainder is excreted as manure or lost to the environment during the production of animal feed (UNEP and WHRC 2007). On the contrary, one study of the Mississippi River Basin estimated that if feed cultivation for meat production were switched to crops that would support a lacto-ovo-vegetarian diet, nitrate exports to the Gulf of Mexico would decrease by 50 % (Donner 2006).

1.3.2.3 Agricultural Extension

In order to fulfill the food demand of increasing population across the globe, the way in which we grow food has changed dramatically. Significant advances in agriculture production have been made, the widespread use of agrochemicals such as synthetic fertilizers and pesticides to improve crop yields. These chemicals and modern machinery allowed the intensification of agriculture, which has led to significant unintended environmental impacts such as nutrient pollution. In fact, agriculture (including livestock agriculture) is the largest source of water pollution. Fertilizer leaching, runoff from agricultural fields, manure from concentrated livestock operations, and aquaculture are the largest agricultural nutrient sources. Between 1960 and 1990, global use of synthetic nitrogen fertilizer increased more than sevenfold, while phosphorus use more than tripled (MA 2005). The excess nutrients are lost through volatilization, surface runoff, and leaching to groundwater. On average, about 20 % of nitrogen fertilizer is lost through surface runoff or leaching into groundwater (MA 2005). Synthetic nitrogen fertilizer and nitrogen in manure that is spread on fields is also subject to volatilization. Volatilization is where nitrogen in the form of ammonia (NH_3) is lost to the atmosphere. Under some conditions, up to 60 % of the nitrogen applied to crops can be lost to the atmosphere by volatilization (University of Delaware Cooperative Extension 2009); more commonly, volatilization losses are 40 % or less (MA 2005). A portion of the volatilized ammonia is redeposited in waterways through atmospheric deposition. Phosphorus, which binds to the soil, is generally lost through sheet and rill erosion from agricultural lands.

1.4 Impacts of Fertilizers on Eutrophication

It is evident that eutrophication is related with a number of anthropogenic activities in urban and rural areas including agricultural practices. Phosphorus and nitrogen input owing to excessive use in agricultural practices, their cycling in the water bodies and seasonal variabilities (temperature, water level, depth, irradiance, and winds) are the main causes of eutrophication (Khan and Ansari 2005). Nonpoint sources of nutrients are often of greater concern than point sources because they are larger and more difficult to control. Fertilizer application on land remains a major contributor to nonpoint nutrient pollution, and this source is still increasing at an alarming rate in many geographic regions (Vitousek et al. 1997). Both industrial and developing nations are using significantly higher loadings of fertilizer in agriculture with global N and P fertilizer usage increasing eightfold and threefold, respectively, since the early 1960s (Constant and Sheldrick 1992; Caraco 1995; Matson et al. 1997; Smil 2001). In addition to compost, several brands of chemical fertilizers containing macro and micronutrients are being excessively used. The fertilizer industry recognizes its crucial role in meeting basic human needs. It stands to meet the challenge of adopting new practices and technologies for greater efficiency and optimum crop productivity to sustain better quality of life (Fixen and West 2002).

The fluxes in nutrient concentration of a water body are the result of synergistic action of population development and fertilizer applications (Caraco 1995; Smil 2001). When these nutrients get to lower rivers, estuaries, and coastal waters, they are available for phytoplankton uptake and growth. The nitrate component of fertilizers can travel long distances. A significant relationship between traveling distance of nitrate and increased phytoplankton productivity was recorded by Mallin et al. (1993). A dramatic trend in world fertilizer production is the increased proportion of urea in world N production, especially in Third-World countries. Urea now comprises roughly 40 % of all N fertilizers produced (Constant and Sheldrick 1992). This is significant because data indicate that in some areas this shift in fertilizer composition has resulted in a shift in the nutrient composition of runoff, potentially favoring some harmful algal bloom species.

In situ experiment of nutrient enrichment in a temperate region reservoir in Seoul (South Korea) revealed that algal response on P treatments were greater than on treatments with $P+NH_4-N$ or $P+NO_3-N$. The response was greater during summer monsoon than in any other season (An 2003).

1.4.1 Effects of Nitrogen

The atmospheric reservoir of gaseous dinitrogen is the initial source of nitrogen. It must be converted by nitrogen fixation

by microorganisms living principally not only in the soil but also in aquatic environments before it is available to most living organisms. In natural water, nitrogen is present as dissolved dinitrogen, ammonia, and salts of the nitrate and nitrite ions.

The supply of both nitrogen and phosphorus from atmosphere deposition is potentially a significant source of nutrients for aquatic ecosystem. However, nitrogen deposition is of higher magnitude than that of phosphorus, it includes dissolved dinitrogen, the products of chemical fixation, and some organic compounds as well. Atmospheric inputs of nitrogen have increased a great deal more than those of phosphorus as a result of human activities. Gaseous nitrogen pollutants may be ammonia from the application of fertilizers and the decomposition of animal and human wastes and oxides of nitrogen from the combustion of fossils fuels and the use of motor vehicles. Such compounds are released into the long-range atmospheric circulation patterns and may travel very long distances, according to atmospheric wind patterns and meteorological conditions, before they are deposited onto a lake surface.

Crop and livestock agricultural systems are important contributors to local, regional, and global budgets of NH_3, NO_X ($NO+NO_2$), and nitrous oxide (N_2O). Emissions of biologically and chemically active NH_3 into the atmosphere serve to redistribute fixed N to local and regional aquatic and terrestrial ecosystems that may otherwise be disconnected from the sources of the N gases. About 50–75 % of N in terrestrial ecosystems emitted from animal excreta and synthetic fertilizer applications (Mosier 2001).

Among nonpoint nutrient pollutions, fertilizer application on land remains a major contributor, and this source is still increasing at a frightening rate in many regions (Vitousek et al. 1997). There is a direct relationship between population development, fertilizer applications, and riverine N and P fluxes (Caraco 1995; Smil 2001). Both industrial and developing nations are using significantly higher loadings of fertilizer in agriculture, with global N usage increasing eightfold, since the early 1960s (Constant and Sheldrick 1992; Caraco 1995; Matson et al. 1997; Smil 2001). These nutrient supplies, after reaching lower rivers, estuaries, and coastal waters, are available for phytoplankton uptake and growth. The nitrate component of fertilizers can travel long distances. Mallin et al. (1993) demonstrated a significant relationship between nitrate, carried ca. 400 km downstream to the lower Neuse estuary (over a 2-week period), and increased phytoplankton productivity. Biological transformations of N added to ponds in the form of inorganic or organic fertilizers and formulated feeds were found to dominate the nitrogen biogeochemistry of aquaculture ponds.

One of the most rapidly increasing sources of nutrients to both freshwaters and the coastal zone is the atmosphere. Nutrient inputs from runoff are influenced by several environmental factors and form of fertilizer in use. A dramatic trend in world fertilizer production is the increased proportion of urea in N production, urea now comprises roughly 40 % of all N fertilizers produced (Constant and Sheldrick 1992). This is significant because data indicate that in some areas this shift in fertilizer composition has resulted in a shift in the nutrient composition of runoff. Nitrate derived from particulate or oxidized nitric/nitrous oxides in wet and dry deposition have long been recognized as important sources of nutrients to streams and lakes, and can be major sources especially for soft water, nutrient-poor freshwater systems (Likens et al. 1979; Kilham 1982). It has been estimated that in estuarine and coastal waters 20–40 % of N inputs can be of atmospheric origin, from industrial, agricultural, and urban sources (Duce 1986; Fisher and Oppenheimer 1991; Paerl 1995; Coale et al. 1996). Interactions of N and iron (Fe) can influence the structure of plankton community (DiTullio et al. 1993) and may act as a regulator of growth and encystment of dinoflagellates (Doucette and Harrison 1991) and possibly in the toxicity of diatoms.

Nearly 81.7 million metric tons of commercial nitrogen fertilizer account for approximately half of all N reaching global croplands now a days and supplies basic food needs for at least 40 % of the world population. The challenge is to meet the increasing food requirements and minimize the risk of negative environmental impacts through improved N-use efficiency. Current N-efficiency and crop productivity are generally lower in several parts of Asia than in North America, but they are improving (Fixen and West 2002).

The surplus nitrogen (N) from Japanese agriculture was speculated to have strongly affected the environment. In a study of N flow in agricultural production during 1980–1997 it was estimated that application of chemical fertilizer per unit area of farmland in Japan peaked in 1985 and then declined. The amount of residual N on farmland (expressed as the difference between N inputs and N outputs) was lowest in 1997 owing to the low input of chemical fertilizers and manure, although the amount of nonutilized livestock waste was highest. Therefore, the total amount of residual N in farmland and nonutilized livestock wastes in Japan were 141, 163, 158, and 148 kg N ha^{-1} in 1980, 1985, 1990, and 1997, respectively (Mishima 2001).

The breakdown of dissolved inorganic and organic nitrogen from readily available compounds such as NH_4^+ and urea was felt to be the important process in the nitrogen nutrient availability. The nitrogen was utilized by the phytoplanktons and bacteria in the Lake Kinneret (Israel), the River Charante estuary, and coastal water near Ile de Re the French Atlantic Coast (Berman et al. 1999).

Nonpoint sources are considered as the major nutrient contributors because they are larger and difficult to control. However, point sources can be a major source of nutrients for small watersheds. Phosphorus and nitrogen in runoff from

agricultural fields are key components of nonpoint source pollution of water bodies and can accelerate eutrophication of surface waters. In an experiment, the fertilizer input with near-surface hydraulic gradient (free drainage, saturation, artesian seepage with and without rain) tested for contribution to the water quality problems. The total NO_3–N loss from free drainage treatment was 0.01 % of the applied N while artesian seepage with and without rain resulted into 16 and 11 % loss of NO_3–N, respectively (Zheng et al. 2004). Sewage from New York City contributes an estimated 67 % of the N inputs to Long Island Sound annually. Sewage treatment plants deliver from 40–80 % of the N to Kaneohe Bay, Hawaii, and to Narragansett Bay, Rhode Island (Nixon and Pilson 1983; National Research Council 1993). It is estimated that sewage contributes only 12 % of the flux of N from the North American continent to the North Atlantic Ocean (Howarth et al. 1996). Only ca. 25 % of the N and P inputs to Chesapeake Bay come from wastewater treatment plants and other point sources (Boynton et al. 1995). Nonpoint source pollution of surface water by nitrate from agricultural activities is a major environmental problem in USA. An agricultural watershed in the Iowa Loess Hills with a 23 years history of annual corn production with average N fertilization has been studied. Head cut seepage was transported through a natural riparian zone and observed as weir base flow; surface runoff was measured separately. The concentration of nitrate carried from the field in basin drainage steadily increased from <1 mg/l in 1969 to >20 mg/l in 1991 (Steinheimer et al. 1998).

The groundwater protection and eutrophication are significant environmental issues on the European agenda. The main source of nitrogen in Europe is leaching from agricultural fields caused by excess fertilizer inputs. Since the late 1970s, nitrate concentrations have increased all over Europe reflecting intensification of agriculture. High nitrate concentrations in ground and surface water make it unsuitable for drinking. High nitrogen inputs in the marine environment cause eutrophication and results in increased algal growth, altered biological communities, and deoxygenation (Iverson et al. 1998). Nitrates from fertilizers account for nearly 50 % of the surface water acidification in watershed. Owing to these N inputs, there is a strong need to cut in NO_X and NH_X emissions (Hessen et al. 1997a, b).

The mathematical model has shown that phosphorus and nitrogen input is likely to be reduced to the extent of 50 and 85 %, respectively into the Swan and Canning Rivers (Australia) provided agricultural land is reforested. The urbanization has also been reported to be a major cause of phosphorus and nitrogen input. During the next 10 years the urbanization is likely to increase 4 and 12 % of phosphorus and nitrogen loads, respectively in the estuary of those rivers (Zammit et al. 2006).

Biological transformations of N added to ponds in the form of inorganic or organic fertilizers and formulated feeds were found to dominate the nitrogen biogeochemistry of aquaculture ponds. Nitrogen application in excess of pond assimilatory capacity can lead to the deterioration of water quality through the accumulation of nitrogenous compounds (e.g., ammonia and nitrate) with toxicity to fish or shrimp (Hargreaves 1998).

1.4.1.1 N-Cycle

Increased use of fertilizers in agriculture has led to the altered nitrogen cycle across the globe. The excessive use of fertilizers increased emissions and transboundary air pollution. During the 1900s, over 50 % of the nitrogen deposition over Republic of Korea (South Korean Peninsula) was imported from abroad. The N inputs from atmospheric deposition, fertilizers, biological fixation, imports of food, feed and products, outputs in riverine export, crop uptake, denitrification, volatilization, runoff, sedimentation, and sea water exchange have been quantified. The nitrogen budgets were found positive with N inputs exceeding outputs. The excess N inputs in turn increased N storage in ground water. Annual accumulation of N in the Yellow Sea including inputs from South Korea and other drainage areas was 1,229 kt per year. The human-derived N inputs lead to excessive eutrophication and pollution of Yellow Sea (Bashkin et al. 2002).

Human activities have greatly altered the global nitrogen (N) cycle and accelerated the rate of N-fixation in landscapes and delivery of N to water bodies. Using data from the early 1990s, Boyer et al. (2002) quantified N inputs in 16 catchments from those of atmospheric deposition, nitrogenous fertilizer applications, biological nitrogen fixation, and imports of N in agricultural products. Net atmospheric deposition was found to be the largest N source (>60 %) to the forested basins of Northern New England. However, in most populated regions of Southern New England, the net import of N in food was the largest N source. The agricultural inputs were the dominant N sources in the mid-Atlantic regions (Boyer et al. 2002).

1.4.1.2 Impact of Phosphorus

Phosphorus (P) inputs are essential for cost-effective crop and livestock agriculture. However, P inputs can also increase the biological productivity of surface waters by accelerating eutrophication that is responsible for the impairment of surface water quality and restricts water use for fisheries, recreation, industry, and drinking because of increased growth of undesirable algae and aquatic weeds and the oxygen shortages caused by their death and decomposition. Phosphorus is mainly responsible for eutrophication of most fresh water around the world (Schindler 1977; Sharpley et al. 1994). Although nitrogen and carbon are also essential to the growth of aquatic biota, most attention has focused on

P inputs because of the difficulty in controlling the exchange of nitrogen and carbon between the atmosphere and water and the fixation of atmospheric nitrogen by some blue-green algae. Therefore, P is often the limiting element, and its control is of prime importance in reducing the accelerated eutrophication of fresh waters.

Agriculture is regarded as an important source of P in environment. However, the rapid growth and intensification of crop and animal farming in any areas has created regional and local imbalances in P inputs and outputs. This has created regional surpluses in P inputs (mineral fertilizers and feed) over outputs (crop and animal produce), built up soil P in excess of crop needs, and increased the loss of P from land to water. Recent research has shown that this loss of P in both surface runoff and subsurface flow originates primarily from small areas within watersheds during a few storms. These areas occur where high soil P, or P application in mineral fertilizer or manure, coincide with high runoff or erosion potential (Sharpley et al. 2001).

Phosphorus is an essential element for all life forms. A mineral nutrient orthophosphate is the only form of P that autotrophs can assimilate (Corell 1998). Phosphorus does not occur as abundantly in soils as N and K. Total phosphorus in surface soils varies between 0.005 and 0.15%. The average total P content of soils is lower in the humid southeast than in the Prairie and Western states. Unfortunately, the quality of total P in soils has little or no relationship to the availability of P to plants. Although Prairie soils are often high in total P, many of them are characteristically low in plant available P. Therefore, understanding the relationship and interactions of the various forms of P in soils and the numerous factors that influence P availability was felt essential to efficient P management (Tisdale et al. 1995).

Anthropogenic factors, viz. mining P and transporting it in fertilizers, animal feeds, agricultural crops, and other products are altering the global P cycle, causing P to accumulate in the soil. Increasing P levels in the soil elevate the potential P runoff to aquatic ecosystems leading to eutrophication of fresh water ecosystems (Schroeder et al. 2004; Djodjic and Bergstrom 2005; Vadas et al. 2005). Phosphorus generally enters aquatic ecosystems adhered to soil particles that are eroded into lakes, streams, and rivers (Daniel et al. 1994; Sharpley et al. 1994). Much of this runoff occurs during major erosion-causing storms (Pionke et al. 1997). Phosphorus-induced pollution of aquatic ecosystems is thus strongly influenced by watershed land use and the concentration of P in watershed soil. Any factor that increases erosion or the amount of P in the soil increases the potential P runoff to downhill aquatic ecosystems (Daniel et al.1994; Sharpley et al. 1994). Most of the eutrophication is caused by water quality problems owing to phosphorus accumulation in upland soils. Accumulation of P in soil and the appearance of adverse effects in freshwater ecosystems may take a long period of many years. Soil P accretion could lead to sudden and unanticipated changes in aquatic ecosystem productivity. It could also cause lags between management actions taken to control eutrophication and the time when results of those actions are realized (Stigliani et al. 1991).

Information regarding human impact on P cycle is meager. However, instances of human impact on the P cycle leading to accumulation of P in upland systems have been discovered. Lowrance et al. (1985) found that imports of P exceeded exports by 3.7 to 11.3 kg ha^{-1} per year in four subwatersheds of the Little River in the Georgia Coastal Plain. Similarly, a P budget of the upper Potomac River Basin revealed that over 60% of imported P was retained within the watershed (Jaworski et al. 1992). In this case, P retention was caused by an excess of fertilizer and animal feed inputs over outputs of agricultural products. In a Florida study, Fluck et al. (1992) found that less than 20% was P output, in agricultural and other products, of P input to the Lake Okeechobee watershed in fertilizers was output. Runge-Metzger (1995) calculated net fertilization (fertilizer input minus crop removal) of 0.7–57.2 kg P ha^{-1} per year in 25 countries of Europe. All the studies showed no country on the globe with net loss of P; all countries were P accumulators. Natural imbalance in P inputs and outputs are not the cause for P accumulation but inputs of fertilizer and animal feeds that exceeded outputs in agricultural products contribute to P accumulation (Runge-Metzger 1995). During 1950 and 1990, an eightfold increase in average available P in the soils of Ireland was recorded (Tunney 1990). In 1990, P inputs in fertilizers to Ireland were more than double the outputs (Tunney 1990). Isermann (1990) calculated the P surplus (total application of fertilizers minus net withdrawal by agricultural products) in the Netherlands and Germany to be 88 and 63 kg ha^{-1} per year, respectively.

Bennett et al. (2001) calculated a global agricultural P budget to determine the amount of P accumulation that occurs in agricultural areas. This budget included only agricultural inputs (fertilizer and manure) and outputs (agricultural products such as meat and eggs, and runoff). Fertilizer inputs were calculated based on global estimates of fertilizer use and P content of fertilizer (FAO 1950–1997). They calculated agricultural P budget from 1958 to 1998 at 5-year intervals, which indicated that the average annual P accumulation in agricultural areas of the world was 8 Tg per year. The result of the study carried out by Bennett et al. (2001) suggest that a considerable fraction of the excess P in the current global budget is being stored in agricultural soils, which occupy 11% of the terrestrial area of the Earth (World Resources Institute 1998).

Moreover, studies predict that fertilizer demand and use will continue to increase to 208 million tons by 2020, with greater increases in developing countries, further aggravat-

ing a trend of freshwater eutrophication worldwide (Bumb and Baanante 1996).

Phosphorus, an essential nutrient for crop and animal production, can accelerate freshwater eutrophication and is considered as one of the most ubiquitous forms of water quality impairment in the developed world. Repeated outbreaks of harmful algal blooms (e.g., Cyanobacteria) have increased society's awareness of eutrophication and the need of solutions. Agriculture is regarded as an important source of P in environment. Specifically, the concentration of specialized farming systems has led to a transfer of P from areas of grain production to animal production. This has created regional surpluses in P inputs (mineral fertilizers and feed) over outputs (crop and animal produce), built up soil P in excess of crop needs, and increased the loss of P from land to water. Recent research has shown that this loss of P in both surface runoff and subsurface flow originates primarily from small areas within watersheds during a few storms. These areas occur where high soil P, or P application in mineral fertilizer or manure, coincide with high runoff or erosion potential (Sharpley et al. 2001).

1.5 Control Measures and Recommendations

Anthropogenic activities are the worst culprit of nutrient enrichment and root cause of eutrophication of water bodies. Several countries have come forward to address the issue by implementing a range of technologies, legislative and biological measures.

1.5.1 Biological Control

Phosphorus (P)-induced eutrophication leads to water quality tribulations in aquatic systems, particularly freshwater, across the globe. Processing of nutrients in shallow habitats removes P from water naturally. Periphytons are considered as one of the tools for P removal from the water column in lotic waters and wetlands. Periphytons play several roles in removing P from the water column, including P uptake and deposition and filtering particulate P from the water. Periphyton photosynthesis locally increases pH up to 1 unit, which can lead to increased precipitation of calcium phosphate, concurrent deposition of carbonate–phosphate complexes and long-term burial of P. In general, periphytons tend to increase P retention and deposition (Dodds-Walter 2003).

Nutrients and food webs have been recorded to have strong interactions which can profoundly alter the eutrophication level of a water body (Hrbâcek et al. 1961; Shapiro 1979; Mazumder 1994; Carpenter et al. 1995; Proulx et al. 1996). The sudden appearance of large populations of herbivorous *Daphnia*, during the recovery of Lake Washington from eutrophication, had profound effects on algal biomass and transparency (Edmondson and Litt 1982; Edmondson 1994). *Daphnia* are efficient grazers capable of clearing the water column of edible algal cells, their appearance caused unexpectedly sharp increase in transparency of Lake Washington (Edmondson 1994).

1.5.1.1 Phytoremediation

In freshwater bodies, the phytoremediation has been suggested to be effective in reducing the toxicity of waters caused by microorganisms releasing ammonia and sulfide during degradation of protein released from food industries.

Several plant species have been found to reduce the excess of nitrogen and phosphorus from aquatic system. Aquatic macrophytes such as *Eicchornia crassipes* and *Salvinia auriculata* cause significant reduction of nitrogen and phosphorus compounds in water. This information was felt helpful in developing adequate management strategy for aquatic macrophytes to check the eutrophication process in Imboassica Lagoon (Petrucio and Esteves 2000). Jiang et al. (2004) reported that *Phragmitis communis* and *Zizania latifolia* have the efficiency to absorbe N and P and thus these two species were found to play an important role in the purification of wetlands receiving nonpoint source pollutants. The harvesting of these species took away 463–515 kg hm^{-2} of N and 127–149 kg hm^{-2} of P each year. This amount of N and P is equivalent to the discharge from 2.3–3.2 and 1.3–3.0 hm^{-2} of fields, respectively in this area. The absorption and decomposition capacity of *Z. latifolia* was higher than *P. communis* (Jiang et al. 2004). Abe et al. (2002) investigated nitrate, nitrite, ammonium, and phosphate ions removal characteristics of aerial macroalga *Trentipholia aurea*. The 1.5 times higher biomass was recorded in medium with sufficient N and P source than in ordinary medium. The macroalga had a potential of 37% of nitrite and 32% of nitrate removal from the wastewater.

Duckweeds have been reported to be promising macrophytes for wastewater treatment. They are used to treat effluent from shrimp farm and found to remove nutrients and high amounts of ammonia effectively (Ruenglertpanyakul et al. 2004). The duckweeds increase the degradation of organic material (Sabine et al. 2003).

Cedergreen and Madsen (2004) investigated the ability and relative contribution of roots and fronds of floating macrophyte *Lemna minor* for N uptake. They showed that roots and leaves of *L. minor* can acquire significant amount of inorganic N through both root and frond.

The wetlands with floating *Lemna gibba* were constructed to treat wastewater from various sources. The suspended solid and organic matter removals were the highest. The nitrogen removal increased with higher nitrogen loads. The phosphorus removal was negligible (Noemi et al. 2004).

1.5.2 Mechanical Control

The problems associated with eutrophication can be overcome by several mechanical means by adopting the strategy of minimum nutrient input and maximum nutrient retention.

1.5.2.1 Fertilizer Requirement

Fertilizers are considered as one of the important sources of nutrients causing eutrophication. Therefore, reducing fertilizer application without compromising the crop requirement by some means could be a strategy to reduce nutrient inputs, of which, use of fertilizer according to the requirements of soil rather than tradition can go far toward reducing nutrient applications in catchments. Optimized use of fertilizer requires regular soil testing so that fertilizer applications are optimized. Soil testing may indicate that some soils with a high P status may be able to do without applications for even longer. Use of an alternative source of fertilizers that could supply phosphorus in a slow release form will be more suitable to the needs of pasture in the high rainfall areas. In addition, particularly for soils with a high phosphorus status, other nutrients such as sulfur and potassium can be used to achieve the most economic level of production (Weaver and Summers 1998). A survey by the South Coast Estuaries Project showed that more than 50% of the soil samples taken in the area had a high P status and could go without extra applications for at least 1 year.

1.5.2.2 Eutrophication Sources and Nutrient Loading

Under natural conditions total phosphorus concentrations in lakes range from 14 to 17 parts per billion (ppb). In 1976, the Environmental Protection Agency recommended phosphorus limits of 25 ppb within lakes to prevent and control eutrophication (Addy and Green 1996). However, many lakes have nutrient levels above this limit. Therefore, to control eutrophication and restore water quality, it is necessary to check and restrict phosphorus inputs, reduce soil erosion, and develop new technologies to limit phosphorus content of over-enriched soils (Carpenter and Lathrop 2008). Methods to control eutrophication include enforcing wastewater treatment and eliminating the importation of chemical phosphorus to watersheds via fertilizers (Schindler 2006).

Hypolimnetic aeration also proved helpful to improve oxygen conditions of water of eutrophic lakes. In hypolimnetic aeration, water from the bottom of a lake is brought to the surface to be oxygenated then returned to the bottom. However, effectiveness of this process is dubious and variable. Studies have shown that this alternative is less effective in shallow lakes and there is little evidence that hypolimnetic aeration reduces algal biomass (Cooke and Carlson 1989). To alleviate eutrophication and algal biomass, regulation of nutrient control focusing on reducing phosphorus input is the most effective way to control eutrophication (Anderson et al. 2002; Smith and Schindler 2009). Lake Washington is perhaps the most widely recognized success story of recovery from eutrophication through nutrient-input control. A considerable improvement of water quality and decrease in phytoplankton was recorded after the diversion of phosphorus-containing wastewater effluent from the lake (Schindler 2006).

Enhanced use of detergents is also one of the major sources of phosphates in enhancing the eutrophication of the water bodies. It has been recorded that phosphorus loads in wastewater fluctuates together with the consumption of phosphate in detergents. Therefore, reduction and eventual elimination of phosphates in detergents would be of prime importance in managing the eutrophication. As synthetic detergents became widespread in the USA since 1970, phosphate consumption raised to a peak of 240,000 t. Although the industries have reduced the amount of phosphate in detergents, but a complete ban would eliminate up to 30% more of the phosphates in sewage, thus reducing future loading to lakes (Litke 1999). Therefore, the need of the hour is to improve water quality by enforcing environmental technology techniques to control discharge from wastewater treatment plants, to find a phosphate substitute in detergents, to educate consumers so that they select washing products with the least amount of polluting components (Knud-Hansen 1994).

1.5.2.3 Nutrient Monitoring and Mathematical Models

Many eutrophication problems can be addressed by preventing the abnormal growth of blue-green and other undesirable algae. One measure for controlling eutrophication is the installation of aeration and circulation equipment, the "Current Control System" that controls the inflow of river and surface water. The efficiency of conventional aeration and circulation is boosted by controlling the vertical distribution of water temperature with this system. Field experiments were carried out on current control in a dam reservoir and the effects of current control to improve the water quality of reservoirs were examined by simulation using a modified one-dimensional model. Parameters of this model were determined by experiments in several reservoirs. The current control system was found effective but its aeration was suggested to be stopped in flood period and turbid water should not be raised to surface when resuming aeration (Niwa et al. 1997).

To control the eutrophication, the phosphorus limitation in surface runoff water may play an important role. In the wetland of Hovi, Finland, the P sorption by Al (ox) played an important role in the first phase of removal of P because wetland retained P efficiently under anoxic conditions. The fine textured mineral soil in the bottom of wetland efficiently retained the P from agricultural runoff (Liikanen et al. 2003).

Removal of harmful algal blooms by chemical treatments may also impair the eutrophication. Sun et al. (2004) used cocamidopropyl betaine (CAPB), a surfactant with high inhibition efficiency, high biodegradability and low cost, to mitigate harmful algal blooms. The half life of the surfactant in sea water was less than 1 day and 90% of the surfactant degraded in 5 days.

HEM-3D (Hydrodynamic-Eutrophic Model-3-Dimensional) Model is a general purpose modeling package for simulation of flow field, transport, and eutrophication processes throughout the water column. The excessive loadings of organic wastes have been found to significantly deteriorate water quality conditions of Korean coastal waters of Kwang-Yang Bay (Park et al. 2005).

Eutrophication, in Lago Maggiore Lake, Italy, was caused by industrial and economic development, the use of P-containing detergents and fertilizers, and the disposal of untreated human sewage into the lakes. Total P concentrations in the lake water increased to 30–35 mg m^{-3}, and a twofold increase in the concentrations of NO_3–N was recorded (Roggiu et al. 1985). More than threefold increase in phytoplankton production was observed, and nuisance blooms of cyanobacteria also occurred (de Bernardi et al. 1996). In order to assess water quality restoration strategies for the lake, Mosello and Roggiu applied the OECD (1982) modeling framework, and they concluded that a 67% reduction in external P loading would be required to return Lago Maggiore from eutrophic to oligotrophic conditions.

To analyze point and diffuse sources of nutrients in Marne river, France over more than 10 years taking into account the role of exchangeable phosphorus, Garnier et al. (2005), applied the RIVERSTRAHLER model (Billen et al. 1994; Garnier et al. 1995; Billen et al. 1998; Garnier and Billen 2002), a generic model of the biogeochemical functioning of whole river systems. Different realistic scenarios of future reduction of phosphorus load were tested, in various hydrological conditions (dry and wet years). They reported that phytoplankton development can be slightly reduced by a further 85% decrease of phosphorus in all the wastewater treatment plants of the basin, but a reduction both of diffuse and point phosphorus sources would be necessary to further decrease eutrophication.

1.5.2.4 Public Awareness and Legislations

Public awareness of the environment shapes the ability to understand the surrounding world, including the laws of the natural environment, sensitivity to all the changes occurring in the environment, understanding of cause-and-effect relationships between the quality of the environment and human behavior, an understanding of how the environment works as a system, and a sense of responsibility for the common heritage of the Earth, such as natural resources—with the aim of preserving them for future generations. The awareness of local people to their surrounding environment and water sources has an important and lasting impact on the environment, and only a cooperative community effort can more efficiently reduce nutrient inputs to water bodies as in the case of Lake Washington, where the reduction in detergent use was the consequence of public awareness. Therefore, it is an urgent need of the hour to increase public awareness and the environmental education of citizens and also develop an integrated strategy to abate eutrophication (Jorgensen 2001).

Australia relied heavily on public education. Two public education campaigns, one within the Murray-Darling Basin in its town called Albury-Wodonga and the other within the Hawkesbury-Nepean Basin in the western suburbs of Sydney, were carried out. The results were positive and it was concluded that campaigns such as "Phosphowatch" can provide a long-term, cost-effective way of addressing eutrophication if the problem is focused at source and a community support is created for an integrated strategy (Howard and McGregor 2000).

There are a number of decision support systems (DSS) that provide advice on the application of inorganic fertilizers and organic manure to farmers. It was suggested that DSS should be based on dynamic models. However, DSS is needed to be developed particularly for organic wastes, grassland systems, and fruits (Falloon et al. 1999).

In 1998, Netherlands government introduced a new manure policy in order to combat pollution of the environment by an excess supply of nutrients in agriculture. This policy is based on a mineral accounting system (MINAS) at the farm level and is focused mainly on nitrogen. MINAS came into force by an alteration of the law on fertilizers. In MINAS, chemical nitrogen fertilizers are included because the use of these fertilizers contributes in the same order of magnitude to nitrogen surpluses as the application of animal manure. It was felt that by implementing MINAS surface waters may eventually be protected against eutrophication and the ground water quality could be improved (Van den Brandt and Smit 1998).

The European Union has taken steps toward the reduction of nitrogen and phosphorous loads in the environment notably through the adoption of several crucial pieces of legislation. A legislative framework has set out to directly tackle the problem of eutrophication through three directives: (1) The Nitrates Directive (1991) aims to protect water quality across Europe by preventing nitrates from agricultural sources polluting ground and surface waters and by promoting the use of good farming practices. (2) The Urban Wastewater Treatment Directive (1991) aims to protect the environment from the adverse effects of urban wastewater discharges and discharges from certain industrial sectors. (3) The Water Framework Directive (2000) lays down a strategy to fight against the pollution of water, including adopting specific measures against pollution by individual pollutants or groups of pol-

lutants presenting a significant risk to or via the aquatic environment.

The regulatory and nonregulatory programs have been developed by the US Environmental Protection Agency (USEPA) to control water pollution. The Clean Water Act defined concentrated animal feeding operations as point sources and all other agricultural sources were considered nonpoint sources and thus not regulated under federal law. There is provision of Coastal Zone Act Reauthorization Amendments of 1990 for nonpoint source management of the USA. For water bodies that continue to be impaired despite the basic implementation of these laws and other programs, states are required to develop a total maximum daily load (TMDL). The TMDL process is the quantitative basis for reaching water quality standards. The USEPA is putting a new emphasis on controlling nutrient pollution sources to meet the goal of the Clean Water Act (Roberta 1998).

1.6 Conclusion

Eutrophication is one of the serious threats to the environment and has heavily degraded freshwater systems by reducing water quality and altering ecosystem structure and function across the globe. Population growth, industrialization, and excessive use of fertilizers are the root cause for disproportionate amounts of nutrients stimulating overgrowth of plants and algae. A solution to eutrophication is urgent since nutrient accumulation renders controlling eutrophication more difficult over time. Whereas the first and most obvious step toward protection and restoration of water bodies is to reduce the nitrogen and phosphorous load to the fresh water systems, which can be done through changes in the agricultural practices, for example, by restrictions in the use of fertilizers, optimizing nutrient use to crop requirements, planning the use of fertilizers, establishment of more sustainable agriculture farms. Moreover, reductions in atmospheric sources of nitrogen, better cleaning of sewage and wastewater, and better control of diffuse urban nutrient sources such as runoff from streets and storm sewers and introduction of wetlands as nutrient sinks can be mentioned as some of the solutions to the eutrophication issues. However, these processes alone are insufficient to produce immediate and long-lasting effects. Therefore, the modern strategies should include many other aspects such as phosphorus enrichment and food web structures to understand the changes that occur after alterations of nutrient loadings. An improved understanding of the interactive effects between grazers, nutrients, and algal production is necessary for successful eutrophication management. Governments should implement more effective policies to regulate the industrial and agricultural sectors to reduce activities that contribute to eutrophication. Finally, it can be postulated that the scientific and public awareness and collective community efforts can play an effective role in reducing nutrient inputs to our vital water bodies.

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Eutrophication: Global Scenario and Local Threat to Dynamics of Aquatic Ecosystems

2

Fareed A. Khan, Fauzia Naushin, Farha Rehman, Ather Masoodi, Mudasir Irfan, Farah Hashmi and Abid A. Ansari

Abstract

All self-regulated aquatic ecosystems maintain their structural and functional dynamics in equilibrium. Most natural oligotrophic surface water bodies maintain production: respiration ratio closer to 1 irrespective of geographical variations. The prevailing environmental gradients govern seasonal, structural and functional dynamics of aquatic ecosystem. During the past century, major socio-economic changes resulted into adverse alteration in both terrestrial and aquatic ecosystems. The terrestrial and aquatic ecosystems are not independent of each other. There is a delicate balance between the two. In the present work, changes in the delicate balance between seasonal, spatial, littoral dynamics and resulting bio-geo-chemical changes in the eutrophic water bodies have been highlighted. Seasonal environmental variables are the forcing factors behind cycling of materials in the water bodies which in turn result into structural and functional dynamics. Summer season triggers the release of orthophosphates bound in the sediments and advection brings the free nutrients to upper water surface and promotes phytoplankton abundance. The rain water input during monsoon may dilute or enrich the water bodies with nutrients subject to the quality of catchment areas. Upwelling and downwelling and surface run offs are among major drivers of the dynamics of water bodies. The hydrological characteristics of water bodies vary with the geographical location. Under extreme polluted conditions, seasonal heterogeneity in nutrient composition of water bodies may not remain maintained except on downstream scale. Phosphorus (P) in runoff from agriculture land accelerates eutrophication of lakes and streams. Seasonal variation of some selected macrophytes in a surface water body close to AMU campus has been studied. About 7.56 ha of catchment area of a nearby park forms a source of fertilizer "run off". Qualitative and quantitative seasonal estimates of density and productivity of two indicator species (*Lemna minor*, *Spirodela polyrrhiza*) and physicochemical properties indicated that the water body is under a fast rate of eutrophication process owing to chemical fertilizer inputs, variables of summer (high wind, high temperature, fast wind speed), winter (low temperature, reduced rain fall), and monsoon (excessive rainfall).

Keywords

Eutrophication · Fertilizers · Nitrogen · Phosphorus · Phytoremediation

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2.1 Introduction

Freshwater is an indispensible resource and essential for life. Freshwater constitutes only 2.5 % of all freely available water on earth's surface, of which only 0.3 % is readily accessible in lakes, reservoirs and rivers (Kalff 2001). Some major problems that humanity is facing in the twenty-first century are related to water quantity and/or water quality issues (UNESCO 2009). The anthropogenic activities result into large-scale contamination or pollution of water. The quality of surface water may degrade if quantities of suspended particles, organic and inorganic substances and microorganisms increase than their usual amounts and hence water becomes unfit for use. "Eutrophication" is the excessive enrichment of surface water with nutrients corresponded by high production of autotrophs, especially algae and cyanobacteria. The high productivity leads to high respiration rates, resulting in hypoxia or anoxia in poorly mixed waters. Low dissolved oxygen (DO) causes the loss of aquatic organism (Corell 1999). The undesirable overgrowth of phytoplankton and their subsequent death forms a greenish slime layer over the surface of water body, which restricts the light penetration (Khan and Ansari 2005, Ansari et al. 2011a, b and c). The death and decay of aquatic plants produce a foul smell and makes the water more turbid (Beeton 2002). Lake Taihu and Lake Baiyandian of China, several Danish lakes, Greek lakes, Lake Chapala of Mexico, Lake Yamoussoukro of West Africa, several water reservoirs and rivers in Asia, Europe, north and south America are highly eutrophic owing to nutrient loads from agriculture households (Jeppesen et al. 1999, Qin 1999, Jose et al. 2000, Raja 2000, Tripathi and Adhikari 1990, Nagy et al. 2002, Huang et al. 2003, Mama et al. 2003, Voutsa et al. 2004, Khan and Ansari 2005, Ansari et al. 2011a, b , c).

In past 30 years, seasonal variations in the characteristics of water bodies have been studied considering a wide range of water quality parameters. The DO in surface water layers and biomass of aquatic macrophytes of fresh water Surinsar Lake (Jammu, India) covaried seasonally (Sehgal and Jyoti 1987). The monsoon seasonality effectively regulated functions and processes of an artificial lentic ecosystem in Seoul (South Korea) and had important implications to eutrophication (An 2003, An et al. 2003). The algal and phytoplankton densities were found mainly related to seasonal water discharge in Rhine and Meuse rivers of Netherlands (Naim 1993, Ibelings et al. 1998). The seasonal variability in number and biomass of zooplanktons corresponded with O_2 availability in a polytrophic Mutek Lake, Poland (Widuto 1988). The seasonal water quality variation in northern coast of Karawang (West Jawa) was directly related with eutrophication. In wet season, excessive input of organic waste with high amount of dissolved inorganic nitrogen and phosphate from agriculture increased chlorophyll-a concentration (Sachoemar and Yanagi 1999). The nitrogen concentration in Yuqiao reservoir basin of China declined in the average flow season near the source and increased in rainy season (Chen et al. 2002). The seasonal changes in summer increased orthophosphate content in Tokyo Bay (Japan) and reflected variations in biological activity (Miyata and Hattori 1986). In Austrian part of river Danube, the seasonal patterns of nutrients were minimum in summer and maximum in winter (Weilguni and Humpesch 1999). The long-term studies of nutrient pattern in Kentucky Lake (USA) revealed that the seasonal variations in nutritional discharge were more pronounced than the actual variation in the reservoir with regulated discharge. Greater variation in the nutrient concentrations were found on eastern forested side of Kentucky Lake (USA) than on agriculturally dominant embayment (Yurista et al. 2004).

Increasing inputs of inorganic fertilizers and pesticides and inefficient use of organic wastes in agriculture adversely affected the biophysical environment creating serious threats to human beings (Mukhopadhyay et al. 2005). Addition of agricultural nutrients (fertilizers) altered the nutrient cycles of watersheds of agro-ecosystems. Nutrients enter the watersheds via precipitation, fertilizers, nitrogen fixation, irrigation, and weathering. The nutrient losses are also derived from stream flow, subsurface flow, deep seepage, and loss of volatile gases as well as the harvest of plants and animal products (Kormondy 2003). Agriculture activities and livestock breeding are the two main nutrient sources responsible for the eutrophication, besides human–urban and industrial wastewater discharges (Sala and Mujeriego 2001).

Accelerated eutrophication of surface waters is often caused by high phosphorus losses from agricultural fields (Sharpley et al. 2001, Schroeder et al. 2004, Djodjic and Bergstrom 2005, Khan and Ansari 2005, Vadas et al. 2005, Ansari et al. 2011a, b and c). In India, the use of fertilizers (urea, phosphate and potash) has increased manifold in the past 40–50 years. A significant quantity of these nutrients reaches nearby water bodies through rain water, irrigation channels and seepage. Flood prone and rainfed water bodies around cultivated areas often show algal blooms. In the present study the seasonal variation in the population of *Lemna minor* and *Spirodella polyrrhiza* and water quality of the Lal Diggi pond, close to the Aligarh Muslim University campus has been studied at monthly interval with special reference to variations in local meteorological variables. The duckweeds are very sensitive to surrounding atmospheric factors. Their potential as indicators of water quality has been studied by several workers (Cheng et al. 2002, Khan and Ansari 2005, Ansari and Khan 2008, 2009, Ansari et al. 2011a, b and c).

2.2 Literature Review

The domestic waste (rich in phosphate and nitrate) when discharged in water bodies makes them highly productive or "eutrophic". Nutrient enrichment is the starting point of eutrophication in any water body and is followed by uncon-

trolled growth of primary producers which depletes oxygen owing to decomposition of algal organic matter. The phosphorous content of eutrophic lakes is between 30 and 100 µg/L and above 100 µg/L phosphorous content is typical of hypereutrophic lakes (Wetzel 2001).

Irradiance and water temperature in summer limited the growth of phytoplanktons in Dokoi Bay of Japan (Morishita et al. 2001). The Hiroshima Bay and Suo Nada of Seto Inland Japanese Sea had significant variation in microbial communities in spring and autumn and corresponded to seasonal changes in sediment parameters (Rajendran and Nagatomo 1999). Two seasonal peaks of the microzooplankton populations, one in the month between late spring and early summer and the other in the autumn season were recorded in highly eutrophic Tokyo Bay of Japan (Nomura et al. 1992). High primary production led to high concentration of particulate phosphorus in surface water of Tokyo Bay which later settled in deeper layers and released orthophosphate on decomposition. This orthophosphate was occasionally advected upwards by wind-induced water mixing and again promoted the phytoplankton growth in upper layers. Increased phosphorus in summer was attributable to increased input from river waters and release of orthophosphate from anoxic sediments (Miyata and Hattori 1986). The phytoplankton standing crop had a high correlation with nutrient loading in three experimental ponds in Japan. The relationship between total phosphorus and chlorophyll-a varied seasonally showing highest correlation in autumn (Aizak et al. 1986). The continuous input of nutrients from the rivers at their confluence with Kasumigaura Lake (Japan) increased algal primary productivity. The particulate matter varied seasonally and maintained higher concentration in Takahamairi Bay than in Tsuchiurairi Bay of the Lake (Ebise 1998).

During wet season, excessive input of organic waste in Karawang, West Jawa increased chlorophyll-a concentration (Sachoemar and Yanagi 1999). The phytoplankton biomass and water quality were influenced by rainfall in Pyeongtaek Reservoir of South Korea (Shin 2003). In Austrian part of River Danube, the concentrations of some nutrients were minimum in summer and maximum in winter (Weilguni and Humpesch 1999). A succession of phytoplankton dominant turbid water from macrophyte dominant clear water state in eutrophic back water of river Denube was recorded between 1992 and 1994 (Kirschner et al. 1999).

In shallow eutrophic Doirani Lake (Denmark), small diatoms (r-species) dominant in the early stage, were replaced by Microcystis, Anabaena and Cerratium (s-species) in summer. Thermal fluctuation and small depth mixing increased sediment-water interaction and altered nutrient concentration (Temponeras et al. 2000). The hydrological conditions in hot season caused eutrophication leading to enhanced algal growth and reduced floral vitality in nutrient-rich degraded reef in France (Naim 1993). The algal growth, rainfall and winds led to nutrient fluctuations over space and time in Messolonghi Lagoon of Greece (Friligos 1989). The wind in shallow lakes played a significant role in seasonal succession (Padisak 1980).

The long-term studies of nutrient patterns in Kentucky Lake (USA) revealed that the seasonal variations in nutrient discharge were more pronounced than the actual variation in the reservoir with regulated discharge. Greater variations in nutrient concentrations were found on eastern forested side of the reservoir than on the western agriculturally dominant embayment. The annual average of nutrient pattern did not change and eventually had no impact on the eutrophication potential during study period from 1989 to 1998 (Yurista et al. 2004).

2.3 Impact of Fertilizers

Phosphorus and nitrogen inputs owing to excessive use in agricultural practices, their cycling in the water bodies and seasonal variability (of temperature, water level, depth, irradiance and winds) are the main causes of eutrophication (Khan and Ansari 2005). The use of fertilizers in agriculture has increased several folds during the past 40 years in India (Anonymous1998, 2002). Several brands of chemical fertilizers containing micro and macro nutrients are being excessively used in addition to compost for optimum crop productivity (Fixen and West 2002). The P-PO_4 concentration greater than 0.1 µg L^{-1} caused eutrophication in three Gorge Reservoirs of China. Nitrogen and phosphorus runoff from agricultural, municipal and industrial effluents increased nutrient input in water (Liu et al. 2004).

2.3.1 Impact of Nitrogen

Commercial nitrogen fertilizers (81.7 million MT) account for approximately half of all nitrogen (N) used in croplands on a global scale. Current N-efficiency and crop productivity are lower in several parts of Asia than in North America (Fixen and West 2002). The application of chemical fertilizer per unit area of farmland in Japan peaked in 1985 (Mishima 2001). Phosphorus and nitrogen in runoff from agricultural fields are key components of non-point source pollution of water bodies and can accelerate eutrophication of surface waters (Zheng et al. 2004). The main source of nitrogen in underground water of Europe is leaching from agricultural fields. High nitrogen inputs in the marine environment cause eutrophication and thus increase algal growth, change biological communities and deoxygenate water (Iverson et al. 1998). Nitrates from fertilizers account for nearly 50% of the surface water acidification in watershed. Non-point source pollution of surface water by nitrate from agricultural activities is a major environmental problem (Steinheimer et al. 1998). Biological transformations of N added to ponds

in the form of inorganic or organic fertilizers and formulated feeds were found to dominate the nitrogen biogeochemistry of aquaculture ponds. Nitrogen application in excess of pond assimilatory capacity deteriorates water quality (Hargreaves 1998).

2.3.2 Impact of Phosphorus

Phosphorus accelerates freshwater eutrophication and water quality impairment. Agriculture is regarded as an important source of P in environment. The loss of P in surface runoff and subsurface flow originates primarily from small areas around watershed, where high application of phosphorus fertilizer or manure coincide with high runoff or erosion potential (Sharpley et al. 2001, Carpenter et al. 1998). In water bodies phosphorus may be present in various forms. All forms of phosphorus are not readily available to plants. Total phosphorus is a measure of all forms of phosphorus (dissolved or suspended) found in any water sample. The soluble reactive phosphorus (SRP) is a measure of orthophosphate. The soluble inorganic phosphorus is directly taken up by plant cells and its concentration indicates the stage of eutrophy and oligotrophy (Hammer 1986). Accelerated eutrophication of surface waters is often caused by high phosphorus losses from agricultural fields (Schroeder et al. 2004, Djodjic and Bergstrom 2005, Vadas et al. 2005). In a German lowland eutrophic river, the clastic sediments acted as P sink in summer when SRP concentrations were relatively high. Organic river substrates serve as phosphorus source (Schulz and Herzog 2004). The application of phosphorus fertilizer and manure increased its transfer potential (Daniel et al. 1998, Zhang et al. 2004). Agriculture and urban activities are major sources of phosphorus and nitrogen to aquatic ecosystems. Nutrient enrichment seriously degrades aquatic ecosystems and impairs the use of water for drinking, industry, agriculture, recreation and other purposes.

The phosphate is relatively immobile element and may be carried to streams through soil erosion and storm runoffs from the excessively fertilized agricultural fields, nurseries, lawns and orchards. Certain synthetic chemicals such as pesticides, construction materials, flame retardants and plasticizers are the other sources of phosphate discharges in freshwater systems (Sharpley 1999). The literature review revealed that surface water bodies around agriculture land, nurseries, cities and fertilizer units are prone to nutrient enrichment which promotes excessive algal blooms. Human interference in up welling and down welling and prevailing climatic factors govern seasonal variations in the population dynamics of the aquatic flora and eutophy of surface water bodies. In the present study, a devastating effect of human interferences on the existence of a small microcosm of a few acres near AMU campus has been studied.

2.4 Material and Methods

2.4.1 Description of the Study Site

Lal Diggi pond is a small rainfed pond located very close on the south of the campus of Aligarh Muslim University, Aligarh, India. Until last two decades, the human settlement around the pond was sparse but now its eastern side is densely populated. The western and southern sides have about 80 and 60 ft wide roads, respectively. In past 20 years, the roads have been raised, which act as weirs and prevents the rain water from its northern, southern and western catchments to drain into the pond. It is a rainfed pond and its water recharging capacity has thus reduced substantially. In 2002, the margins of this pond were raised again and a bypass drain constructed around its coastal lines took the rain water of its catchments away from this pond. The water level consistently reduced during 2002 and 2003. On realizing this disastrous change, the pond finally dried by May 2004. The pond was later on refilled and a passage for rain water unloading was reconstructed in 2005. The devastating changes in the physico-chemical property of the pond and seasonal variations were studied as described in the following section.

2.5 Results

2.5.1 Monthly Qualitative Studies

April 2003 The water level in the pond at various places varied between 2 and 4 feet. About 7–8 m wide moist and marshy northern coastline was occupied by *Typha angustata*. Eastern marshy coastlines (18–20 ft wide) had relatively denser population of *Typha angustata*. A patch of *Paspalum paspaloids* occupied 12–15 m wide area of the water body in the southern margin. South-western side had a patch of *Typha angustata* and remaining western side of the pond was open. Thus, the existing water body was surrounded by *Typha angustata* from northern, eastern and south western sides and by *Paspalum paspaloides* from the southern side. The main water body on its eastern margin was covered with mature water hyacinth (*Eichhornia crassipes*) almost in drying stage. The open area of water body was covered with duck weeds on the western side and south western side. The duck weeds were in the mature stage and at places most of them dried and formed slime body. About 50–100 cm of water level was recorded at about 5 m inside of the western coast of this mesocosm.

May 2003 The duckweeds on the western side of the pond dried almost completely. The water level in this area of the pond was maintained between 50 and100 cm. The water hyacinth on eastern side completely dried. The *Typha angustata*

and *Paspalum paspaloides* occupied larger area on its northern and southern margins (Plate 1). But their density reduced in the harvested areas on southern side. *T. angustata* and *P. paspaloides* are harvested at small scale by local farmers and used for making mats and cattle feed.

June 2003 The size of water body reduced in area. The water depth varied from 25 cm to a little over 60 cm. The duckweeds and water hyacinth disappeared. The patches of *Typha angustata* expended from moist eastern coast to the centre of pond. The water depth reduced to 12–15 cm on northern coast. The density of *T. angustata* further reduced owing to intensive harvesting. The *T. angustata* on eastern side was in drying phase but relatively green on south western side. The water receded and left eastern and northern sides as exposed moist sediments. About 20–30 m of southern coastal side of water body further dried and turned to be a marshy area.

July 2003 The pond was recharged owing to downpour in its catchment. The water level increased up to 90–110 cm with lesser density of duckweeds. The *Spirodela polyrrhiza* was more abundant (+++) than *Lemna minor* (+). The *Typha angustata* started sprouting again. The dried margins along all its sides, recorded in preceding month became marshy again. The water body swelled by the end of July 2003. The water-filled area and depth of the pond increased. The duckweeds covered the water surface within and between the patches of *Typha angustata* in the centre, eastern, northern and south western sides of the pond.

August 2003 Most of the water surface was covered with duckweeds (*Lemna minor* and *Spirodelapolyrrhiza*). The density of duckweeds increased in this month as compared to July 2003. The water level increased up to 90–150 cm. The density of *Lemna minor* (+++) and *Spirodela polyrrhiza* (++++) increased as compared to the last month. The water-filled area of the pond was almost one and a half times larger than in the July 2003. The density of the *T. angustata* on eastern and southern coasts increased. The central part of the pond was free from any floating, submerged or rooted submerged plants. In this month, some diatoms and blue-green algae (details not covered in this study) were also noted to be present on coastal sides.

September 2003 Water level and area of the water body continued to be very high. The water depth was 100–150 cm on southern and eastern coast of the pond. The density of *Lemna minor* and *Spirodela polyrrhiza* decreased as compared to the density recorded in August. For the first time, some small patches of *Wolffiaarrhiza* were also noted on the shallow coastal sides of the pond. The blue-green algae and diatoms were present.

October 2003 The water level at some places receded. The area of water body reduced. The water depth receded up to 30–50 cm on eastern southern and western coasts. The total area and volume of the water body reduced as compared to September. The density of *Lemna minor* and *Spirodela polyrrhiza* reduced substantially and disappeared from a large portion of the water body. The duckweeds were limited in 4 m × 6 m size patches in open water area and between the patches of *Typha angustata* on the eastern and south western sides. Some small patches of *Wolffia arrhiza* were also present.

November 2003 Both the selected duckweeds (*Lemna minor* and *Spirodela polyrrhiza*) rebloomed on the margins of open water body. The central part of the water body was almost devoid of duckweeds. Sparse populations of *Wolffia arrhiza* in small patches of approximately 25 × 30 cm to 50 × 50 cm sizes were found on the shallow and marshy margins of pond. The presence of algae and diatoms caused greenish appearance of water on the north western and western coasts of the pond.

December 2003 The duckweeds disappeared leaving the water surface open. The *Typha angustata* bloomed on north eastern, eastern and south western sides of the pond. *Paspalum paspaloides* grew predominantly on southern side. The water in this month was more turbid and dirty owing to the decaying duckweeds. The area of water body reduced slightly.

January 2004 The duckweeds started reappearing with abundant *Spirodela polyrrhiza* (++) and sparse population of *Lemna minor*. Dense patches of *Paspalum paspaloides* were recorded. The water body size reduced further than in the month of November and December. The north western side of the pond turned marshy and at places, patches of sediments were exposed. The main water body was limited to central and western side of pond. Rare occurrence of *Eichhornia crassipes* was seen on the eastern and north eastern margins. The water was more turbid than in the preceding month.

February 2004 The population of duckweeds was dense owing to gregarious blooming. The water level and area reduced further. The water was turbid. The density of water hyacinth was relatively higher than in the month of January.

March 2004 The major part of the water body was covered with densely populated duckweeds (*Lemna minor* and *Spirodela polyrrhiza*). A dense semi-lunar stripe of water hyacinth was formed and floated along northern, eastern and southern coasts. The water hyacinths were in the stage of drying. The patches of mature duckweeds formed thick brownish

mat. The area and volume of water body reduced further and eventually, the duckweeds and water hyacinth formed a thick cover on almost entire water surface.

April 2004 The duckweeds and water hyacinth were relatively denser than in April 2003, but in drying stage. The size of the water body was far smaller and limited to central and western side of the pond. Owing to fast reduction in water level and almost no recharging with the rain water, a vast area of the pond had several smaller patches of *Typha angustata* even in the centre of the pond. The pond dried by the end of May 2004. Sedge grass showed slight browning as it started drying after the maturity. Considerable drying of duckweeds was recorded along its coast and in the central part of very small patch of water body. The water level of 30–60 cm hindered the movement of small boats. Larger area sediment was exposed at many places (Fig. 2.1)

The aquatic body turned into terrestrial body and by April 2005, some trees of *Acacia nilotica* and *Prosopis* species appeared on the eastern, and northern and in the centre of the dried pond. In the following monsoon (July 2005–August 2005), the district local authorities managed the refilling of the pond with fresh water and reduced the weirs around it. This unusual restoration management resulted into a better non-blooming and lesser eutrophic water body.

2.5.2 Quantitative Studies

The monthly data on seasonal variation in population dynamics of *Lemna minor* and *Spirodela polyrrhiza* in the rainfed Lal Diggi pond is summarized in Table 1. Both the duckweeds had numerical dominance in the months of February and March. *Lemna* bloomed in the months of November and August. *Lemna* and *Spirodela* did not grow in summer (April to June) and December. The density of *Lemna minor* dropped down significantly to 1,182 individuals/m^2 and of *Spirodela polyrrhiza* to 2,358 individuals/ m^2 area of the pond. The highest fresh weight of the selected macrophytes along with blue-green algae and other floating macrophytes (excluding water hyacinth) was recorded in the month of November 2003, March 2003, August 2003 and February 2004. The fresh biomass was minimum in the month of January (Table 2). *Spirodela* accumulated maximum dry matter in the month of February 2004 followed by March 2003, November 2003 and August 2003. *Lemna* accumulated maximum dry matter in the month of March 2004 followed by November, February and August of previous year (2003). The dry weight of *Spirodela* and *Lemna* was least in the month of January 2004 and September 2003, respectively. The net primary productivity (NPP) of both the duckweeds was high in the months of February 2004, August 2003 and November 2003 (Table 2.1).

Spirodela polyrrhiza 225.82 g $m^{-2}yr^{-1}$ The data in Table 2 show monthly variations in the population of *Lemna minor, Spirodela polyrrhiza, Wolffia arrhiza* and chemical characteristics of water (pH, NPK, TDS, turbidity) of the selected mesocosm, average atmospheric temperature and precipitation (rainfall in mm). *Lemna minor* and *Spirodela polyrrhiza* bloomed between July 2003 and March 2004 (except in December 2003). The occurrence of duckweeds was recorded in April 2003. The pH, water turbidity, total dissolved salts (TDS) and NPK contents were high but dissolve oxygen was very low in summer (April 2003 to July 2003). The nutrient contents (NPK) increased as the volume of water reduced in summer. The pH and turbidity reduced as the water body swelled after 11.4 mm downpour in the month of July (Table 2.2).

Lemna minor and *Spirodela polyrrhiza* bloomed in July 2003. The population ratio of *Lemna:Spirodela* was approximately 18:6 (105:36 individuals of *Lemna* and *Spirodela* respectively). The density of both these duckweeds increased in the month of August 2003 (Table 2). In this month the pH, turbidity and nutrients of the water decreased owing to recharging with rain water (causing natural dilution) and binding of nutrient into blooming aquatic organism. In September 2003, the population of duckweeds decreased substantially and few small patches (1–2 ft^2) of *Wolffia* appeared. The population of *Lemna, Spirodela* and *Wolffia* continued to bloom untill November. In the entire study period, the *Lemna:Spirodela* ratio varied between 18:6 and 24:6. The water pH reduced in November. The duckweeds dried and disappeared in December 2003. *Lemna* and *Spirodela* reappeared and bloomed in the month of January 2004. The turbidity, NPK and pH increased from December 2003 onwards. The highest population ratio between *Lemna* and *Spirodela* was recorded in November 2003, February 2004 and July 2003. In the month of April 2004, the duckweeds and other floating macrophytes such as *Eicchornia crassipes* (not covered in the present study) died. The water level also decreased sharply. The major part of the pond on eastern, southern and northern sides dried up first and completely by the end of May 2004. The pond remained dry for several months and could be recharged after the hurdles (weirs) around the pond were partially removed to let the mesocosm receive the rain water from its catchments.

2.6 Discussion

In the beginning of summer (April 2003), the size and volume of the main water body of "Lal Diggi" reduced with dirty appearance of water and moist or marshy margin around the pond with dense population of *Typha angustata* and *Paspalum paspaloides*. The water body size further reduced in May 2003 (Table 1). Rainfall in these 2 months

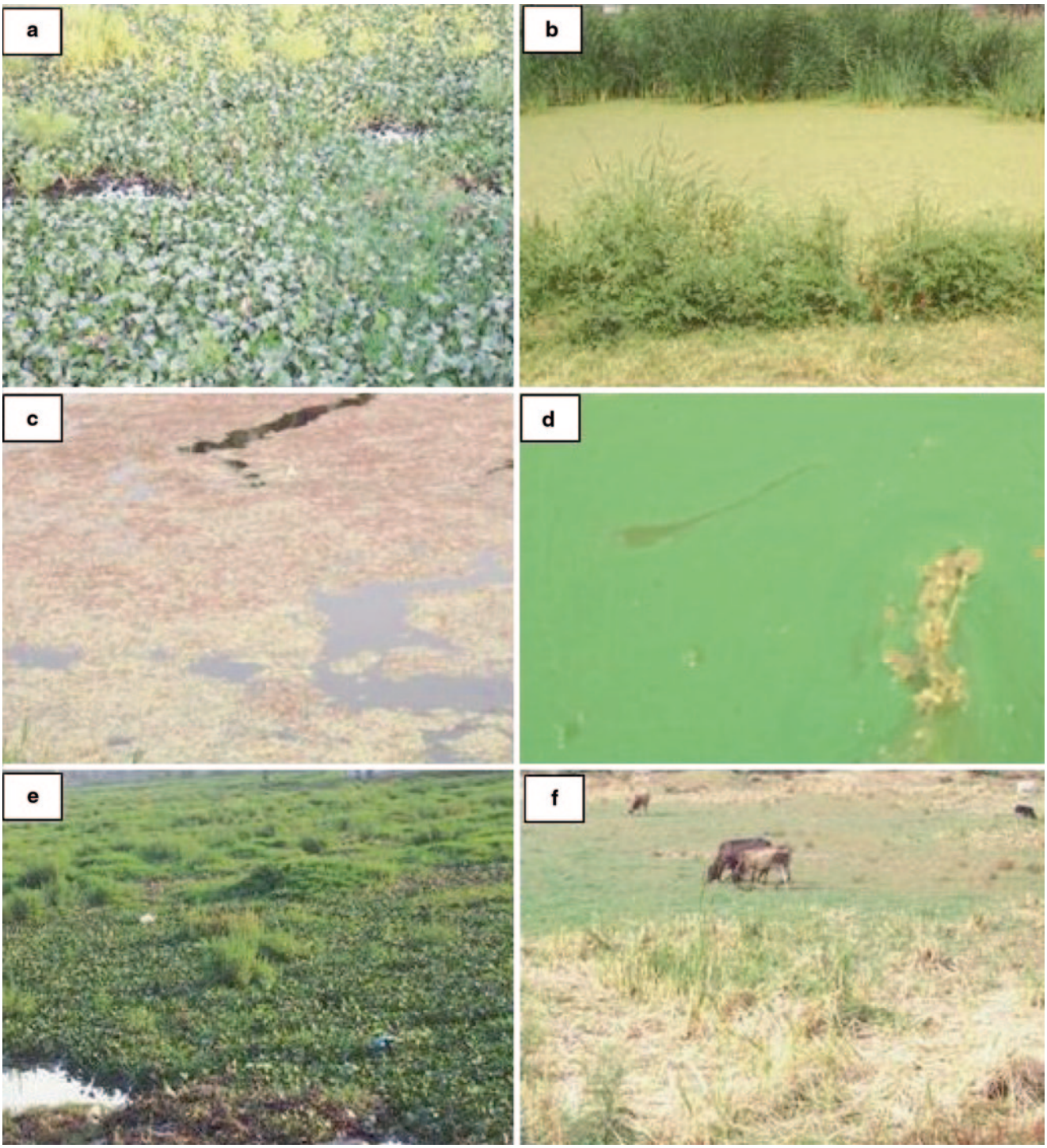

Fig. 2.1 Population of *Eichornia crassipes* on eastern side of the pond (**a**), Blooming of duckweeds (*Lemna* and S*pirodela*) in the open part of western side (**b**), Duckweeds in the drying stage (**c**), Algal bloom in small patches (**d**), *Eichornia crassipes* and *Paspalum paspaloides* (**e**), Dried part of the pond in May 2004 (**f**)

was very low and average temperature and pH were very high (Table 2). The duckweeds in these two summer months did not survive. It is likely that reduction in area, depth and volume of water body in the summer may have increased turbidity and nutrient concentrations in the water body. The nutrients bound in the plants were released after decay of duckweeds and advected to upper surface in summer. High pH, nutrient, turbidity and temperature were feasibly far above the optimum requirement of the duckweeds and may have increased their mortality. In microcosm experiments,

Table 2.1 Seasonal variations in the population dynamics and Net Primary Productivity (NPP) of selected floating macrophytes (duckweeds) in Lal Diggi pond near University campus

Month	Total fresh weight (g m^{-2})	Plant	Population (×1,000 m^2)	Fresh weight (g m^{-2})	Dry weight (g m^{-2})	NPP (g m^{-2} d^{-1})
April 2003	–	–	–	–	–	–
May	–	–	–	–	–	–
June	–	–	–	–	–	–
July	448±24.1	L	9.47±0.08	116.48±4.11	12.79±0.05	+0.43
		S	3.25±0.05	135.29±1.55	17.23±0.08	+0.57
August	1,508±189.9	L	41.53±0.09	485.58±5.22	61.32±0.06	+1.57
		S	15.68±0.03	672.57±18.83	79.02±0.14	+1.99
September	1,108±188.7	L	8.35±0.02	95.29±9.9	11.68±0.03	−1.60
		S	8.71±0.03	385.58±15.98	42.77±0.10	−1.17
October	516±51.6	L	15.79±0.04	181.63±4.17	23.71±0.08	+0.40
		S	6.64±0.06	262.13±8.06	31.79±0.09	−0.37
November	1,732±159.8	L	63.84±0.06	730.90±48.49	84.18±0.08	+1.95
		S	15.83±0.02	710.12±74.32	81.16±0.05	+1.59
December	–	–	–	–	–	–
January 2004	300±40.9	L	1.18±0.02	136.20±4.20	1.44±0.04	+0.05
		S	2.36±0.05	100.80±1.04	12.24±0.09	+0.39
February	1,476±185.4	L	64.65±0.08	729.14±36.67	84.13±0.10	+2.67
		S	19.09±0.03	619.92±49.13	97.33±0.15	+2.74
March	1,680±106.0	L	65.62±0.09	735.84±45.12	97.88±.16	+0.49
		S	18.72±0.02	692.16±30.49	94.18±0.08	−0.11

Annual Production: *Lemna minor* 231.70 g m^{-2} yr^{-1}

high NPK concentrations reduced the population growth of *Lemna minor* and *Spirodela polyrrhiza* (Hashmi 2006). The nutrient availability directly affects natality, mortality, density, growth pattern, life form, longevity and age structure of the plant population (Kormondy 2003).

The optimum concentrations of NPK usually influence natality, mortality, density and growth of plants. The concentration of the nutrients below and beyond the ecological amplitude may have influenced most or all these characteristics adversely. Laboratory experiments revealed that high NPK concentration induced early mortality and lower concentrations increased natality of *Lemna and Spirodela* (Hashmi 2006). Morishita et al. (2001) noted that high irradiance and water temperature in the month of summer hampered the growth and biomass of phytoplankton in Dokai Bay of Japan. In Tokyo bay (Japan), an oscillatory high and low particulate phosphorus and ortho-phosphorus was recorded. The wind speed in summer advected and mixed up the nutrients of sediments and upper and lower water layers which in turn altered the water quality parameters (Miyata and Hattori 1986). Alterations in water quality and related seasonal variability of phytoplankton and zooplankton have been noted in fresh and marine water ecosystem from various parts of Asia (Emir and Demirsoy 1996, Shin 2003). In a degraded reef, the hydrological condition in hot season caused eutrophication and reduced floral vitality (Naim 1993). Algal rain and wind caused nutrient fluctuation and thereby altered salinity, DO, nutrients and chlorophyll-a in the Messolonghi Lagoon of Greece (Friligos 1989). The harvesting of *Typha angustata* as cattle feed transferred part of nutrients bound in organic form back to terrestrial environment. Consistent removal of aquatic plants from spring fed stream in Hiroshima (Japan) receiving sewage input paved the way for seasonal peaks in population of microzooplanktons in early summer (Nomura et al. 1992). In rainy season (July and August), the size of the selected rainfed water body swelled leading to the bloom of *Lemna minor* and *Spirodela polyrrhiza.* In September 2003, the density of duckweeds decreased marginally. There was adequate rainfall in September 2003. Seasonal monsoon rain modifies chemical and biological characteristics of an artificial lentic ecosystem. Monsoons regulate function and processes of water body and eutrophication (An et al. 2003). The pH, turbidity and biological characteristics of the present body may have changed in the month of September 2003 with consistent rainfall. The precipitation in the form of snow during December and March and anthropogenically increased water level in some lakes of Poland influenced water qualities (Gorniak and Piekarski 2002).

The atmospheric temperature in winter (October to December 2003) consistently decreased around the selected pond, but size of the water body did not reduce much. Some small patches of *Wolffia arrhiza* occurred from October to December 2003 on shallow margins of the pond which might have been introduced in the water body accidentally through predatory birds.

The death and decay of duckweeds and diatoms in December 2003 corresponded with the increase in the turbidity of pond water as was also noted in an eutrophic shallow lake

Table 2.2 Relative proportion of the occurrence of selected duckweeds, physico-chemical characteristics of water, atmospheric temperature, monthly precipitation and wind velocity in Lal Diggi pond

Month	L:S ratio** (Number)	*Wolffia* occurrence (Number)	pH	Turbidity	Dissolved oxygen (mg L^{-1})	Total dissolved salts (mg L^{-1})	Nitrate (mg L^{-1})	Phosphate (mg L^{-1})	Potassium (mg L^{-1})	Rainfall* (mm)	Average atmospheric* temperature (°C)		Average wind velocity* (km h^{-1})
											Min.	Max.	
April 2003	–	–	7.7±0.3	25±2.6	3.60±0.21	2,290±512	0.8±0.3	3.9±0.16	23.7±1.9	3.2	20.6	36.6	7.920
May	–	–	8.1±0.4	24±3.3	3.30±0.18	2,361±407	11.2±0.6	3.8±0.17	24.6±2.8	2.0	25.3	40.0	8.237
June	–	–	8.1±0.4	25±4.4	3.60±0.17	2,416±506	11.3±0.7	3.6±0.16	24.3±3.1	10.0	25.8	38.1	8.870
July	105:36	0	7.6±0.34	20±2.7	4.60±0.18	1,933±461	11.3±0.3	3.5±0.21	20.3±1.3	11.4	2.64	36.9	7.286
August	138:52	–	7.1±0.39	18±2.1	5.60±0.27	1,763±498	9.8±0.6	2.8±0.13	19.6±1.8	277.2	25.0	32.2	6.494
September	37:39	20	7.3±0.3	17±2.2	5.58±0.31	1,952±524	9.3±0.3	2.4±0.12	23.1±1.8	117.9	23.7	34.1	6.178
October	153:64	43	7.3±0.2	19±2.5	5.11±0.22	2,061±318	9.8±0.2	3.6±0.11	24.6±2.6	95.0	18.6	30.3	4.910
November	184:45	47	6.8±0.3	20±3.8	4.80±0.18	1,822±276	9.8±0.3	3.1±0.14	23.3±2.1	–	11.5	27.9	4.594
December	–	–	6.9±0.6	21±4.0	3.30±0.21	1,890±386	9.8±0.6	3.2±0.13	20.6±3.2	–	8.0	17.2	4.752
January 2004	19:39	–	6.9±0.3	21±3.8	3.60±0.23	2,013±427	10.1±0.4	3.1±0.16	20.3±3.1	11.7	7.1	15.6	5.227
February	219:65	–	7.3±0.2	22±3.7	3.70±0.18	1,682±366	10.3±0.5	3.6±0.14	19.6±2.8	–	9.8	23.3	5.544
March	195:55	–	7.3±0.2	23±3.9	4.20±0.13	1,631±402	10.5±0.3	3.8±0.11	22.5±2.2	–	15.7	32.4	6.811
April	–	–	7.6±0.4	26±2.8	–	–	–	–	–	–	21.9	38.0	6.860

*Courtesy: Meteorological Survey of India, Govt. of India

**Median of the number of each species in 3 quadrats of 25 × 10 cm^2 approximatelyWithin parenthesis numerical ratio of L:S each quadrat against a fixed number (6) of *Spirodela polyrrhiza* individuals

(Temponeras et al. 2000). Consistent and rapid reduction in size and depth of the pond was recorded from January 2004 to April 2004 which finally dried in May 2004. Despite sufficient precipitation in the month of January, the water body could not be charged with rain water from its catchments owing to anthropogenic reasons (development of weirs around the pond). Therefore, the size of this rainfed water body continued to decrease with rise in temperature and wind speed from January to April 2004. Consistent reduction in the size of water body, increase in temperature, wind speed, irradiance and failure in water recharging may have also increased turbidity, pH, nutrient and water temperature. These factors may not have been conducive for the growth of duckweeds in these months (January to April). Past studies have revealed that bio-physico-chemical factors and seasonal dynamics influenced the flora of water bodies (Wulff 1980, Friligos 1989, Christensen et al. 1990, Talling 1992, Koening et al. 1995, Nogueira et al. 1997, Havens et al. 1999, Kirschner et al. 1999, Weilguni and Humpesch 1999, Temponeras et al. 2000, Dodds-Walter et al. 2002, Artioli et al. 2005, Khan and Ansari 2005, Ansari et al. 2011a, b and c). Therefore, anthropogenic alteration and climate influence the physico–chemical property of water and flora of the water body leading it to eutrophy.

2.7 Conclusion

The fresh water lakes and ponds in many Indian cities are source of fresh water for various purposes. The surface water bodies recharge the underground water resource. The nutrient enrichment of surface water bodies and formation of weirs inhibiting the water recharging may onset an early natural succession. The collection of rain water in such water bodies must be an essential part of city planning and water management.

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Effects of Eutrophication

3

Mohamed M. Dorgham

Abstract

Eutrophication as one of the importunate environmental hazards in the aquatic ecosystems causes pronounced deterioration of the water quality and represents serious threat to the biotic components of this ecosystem. The main environmental effects of eutrophication are increase of suspended particles owing to extensive macroalgal blooms, decrease of water clarity, and increase in the rate of precipitation that led to the destruction of benthic habitat by shading of submerged vegetation. In addition, other important effects are also known such as the bottom-water hypoxia, production of CO_2 associating the decomposition of intensive produced organic matter which enhances water acidification, and altering biogeochemical processes, including sediment anoxia, accumulation of deleterious hydrogen sulfide, and nutrient cycling. Shift in the phytoplankton community was frequently reported in numerous eutrophic coastal waters owing to the variable nutrient requirement of different phytoplankton groups and the ratios between the different nutrients in these waters. Eutrophication is often accompanied by algal blooms which are frequently harmful and cause various injuries to the aquatic animals, such as clogging of fish gills, poisoning by toxins secretion, and localized anoxia, which consequently lead to detrimental effect on the fishing resources and the national economy through mass mortality of variable aquatic animals.The hypoxia conditions in bottom waters cause escape of sensitive demersal and other benthic fishes, mortality of bivalves, echinoderms and crustaceans, and extreme loss of benthic diversity, which led to changes in the diet of bottom-feeding fishes as well as shift in dominance among demersal fish species. Increase of algal growth/organic production rates led to changes in the benthic community structure, such as replacement of hermatypic corals with coralline algae, filamentous algae, macroalgae, and/or a variety of filter feeders and increase of bioerosion in some forms. Trophic linkages between pelagic and benthic communities are affected by eutrophication in the coastal waters, where the feeding habit of higher consumers such as benthic fish changes to derive high percentage of their energy from pelagic primary production sources. Shellfishes as an intermediate link between the water column and demersal fish could also be affected by eutrophication and will impact (as prey) on the demersal fish production. Meanwhile, increasing turbidity with eutrophication led to a shift in fish species owing to change of feeding on zooplankton to benthic organisms. Severe shading and light attenuation caused by blooms of both macroalgae and phytoplankton in eutrophic conditions hinder the photosynthetic processes in benthic plants and has led to the decline of seagrass habitats. High nutrient levels may lead to disturbance

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in nitrogen and phosphorus metabolism in seagrass and consequently cause a change in plant communities. Coral reefs are affected by eutrophication in different aspects. The organic compounds released from algal blooms promote microbial activity on coral surfaces and cause coral mortality, while synergistic effect of both the dissolved organic matter and rates of bioerosion has a pronounced role in reef degradation. Harmful algal blooms caused a complete loss of the branching corals, and substantial reductions in the abundance, richness, and trophic diversity of the associated coral reef fish communities. Eutrophication and siltation have severely stressed many fringing and offshore reefs that prefer to grow in nutrient-poor waters, and cause physiological changes in growth and skeletal strength, decrease of reproductive effort, and a reduced ability to withstand disease. In many marine eutrophic habitats, zooplankton community experienced a decline in species richness and abundance, change in structure, size, reproduction rate, and feeding habits. Size change in zooplankton occurs owing to the replacement of small species by another relatively large species of the same group, while the structure may change because of the trophic relationship of zooplankton with their prey (primary producers) and predators (fishes). Although benthic foraminiferans have been widely used as indicators of eutrophication in coastal marine ecosystems, low species diversity and high population densities of several benthic foraminiferans were reported in eutrophic area. On the other hand, smaller opportunistic benthic foraminiferal species dominate in the coral reef ecosystems and lead to a decline of larger endosymbiont-bearing taxa, while the hypoxia-tolerant foraminiferan species increased in abundance against the disappearance of the more sensitive species.

Keywords

Benthic life · Coral reefs · Eutrophication · Harmful algal blooms · Phytoplankton · Seagrasses · Trophic linkage · Zooplankton

3.1 Introduction

Eutrophication is a complex process which occurs both in fresh and marine waters, where excessive development of certain types of algae disturbs the aquatic ecosystems and becomes a threat to animal and human health (European Communities 2002). It is one of the most anthropogenic sources of hazardous effect on the aquatic ecosystems. Several definitions of eutrophication have been proposed. For example, eutrophication is defined as an increase in the rate of supply of organic matter to an ecosystem, which is typically reflected by an increase in the primary production of the system (EEA 2001). It is the enrichment of water by nutrients, especially compounds of nitrogen and phosphorous, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and the quality of the water (CEC 1991). Two criteria for the evaluation of eutrophication are known; the first, applied in European countries, is based on nutrient concentrations to differentiate between two conditions of the water quality: poor and bad (EEA 1999), and the second criterion, applicable in USA, is based on high chlorophyll *a* and low oxygen saturation (Bricker et al. 1999).

The threat of eutrophication was first reported in freshwater ecosystems (Vollenweider 1976), and later, since the early 1970s, in the coastal and marine ecosystems (Smith 2006). Numerous parts of the world marine habitats suffered from acute eutrophication, for example, Chesapeake Bay in USA, Inland Sea of Japan, the Black Sea, Chinese coastal waters (Anderson et al. 2002), and southeastern Mediterranean (Dorgham 2011). It is among the most detrimental of all human activities in coastal ecosystems (Heckjr and Valentine 2007), causing coastal hypoxia and food-web-altering in many threatened areas (Levin et al. 2009).

Eutrophication as an environmental problem is distributed worldwide; within a few decades, numerous pristine, oligotrophic estuarine, and coastal waters have transformed to eutrophic conditions, which, in several occasions have been accompanied by epidemic harmful algal blooms (HABs; Smayda 1990).

The effect of eutrophication is not restricted only to the biological and ecological characteristics of the aquatic habitat, but may extend to cause severe social-economic losses (Kumagai 2008). The deleterious effects of eutrophication on the abiotic and biotic ecosystems will be discussed in the following parts.

3.2 Effects on the Ecosystem

The impact of eutrophication could appear on variable aspects and characteristics of the ecosystem including biotic and abiotic components. Coastal marine communities are being increasingly affected by disturbance events (Thompson et al. 2002) such as the fast-growing phytoplankton, microphytobenthos, ephemeral macroalgae (Borum 1996), and increase of suspended particles in the sea water which are trapped on the sea bottom and caused loss of submersed macrophyte beds (Rybicki et al. 1997). The suboxic conditions may enhance intensive growth of filamentous bacteria on the sea bed which oxidizes sulfide, providing a detoxified microhabitat for eukaryotic benthic communities (Levin et al. 2009), while the intensive algal growth resulting from nutrient enrichment causes replacement of hermatypic corals with coralline algae, filamentous algae, macroalgae, and a variety of filter feeders (Foden et al. 2011).

In Chesapeake Bay, bottom-water hypoxia resulted in diminished submerged aquatic vegetation and fisheries harvests (Flemer et al. 1983) and a steady decline of abundant native oysters, *Crassostrea virginica* (Kirby and Miller 2005). In Skagerrak (Sweden) and Kattegat (Denmark) of the North Sea, increasing eutrophication during the last 15–20 years accompanied by oxygen decrease (Andersson and Rydberg 1993) reduced the growth depth of macroalgae and caused an increase in biomass and change in the species composition in benthic communities (Anon 1993). The disastrous bloom of the prymnesiophyte *Chrysochromulina polylepis* occurred in the Skagerrak-Kattegat area during spring 1988 (Ambio 1990) and caused fundamental ecological changes (Graneli and Risinger 1995). Meanwhile, in the inshore regions of the Great Barrier Reef, acute eutrophication increased environmental risk probabilities on the ecosystem health (Brodie 1997).

Accelerated eutrophication poses a serious threat to the long-term health and function of many coastal bays in the mid-Atlantic, impacting essential habitats (e.g., seagrass and shellfish beds) as well as finfish nursery areas (Kennish 2007). Also, high levels of algal growth were reported in these shallow bays, accelerating seagrass loss, increasing system respiration and oxygen stress, and altering biogeochemical processes (e.g., sediment anoxia, accumulation of deleterious hydrogen sulfide, and nutrient cycling) that are detrimental to ecosystem structure and function (Kennish 2009), in addition to nuisance and toxic algal blooms (HABs), loss of submerged aquatic vegetation, altered benthic faunal communities, and impacted essential habitats and harvestable fisheries (Valiela 2006).

High production of CO_2 associated with the decomposition-intensive organic matter produced in eutrophic areas enhances water acidification. In the northern Gulf of Mexico and the East China Sea, CO_2 produced during the decomposition (microbial respiration) of lush organic matter resulting from eutrophicated river plumes, has already enhanced the acidification of coastal subsurface waters (Minhazul Islam 2011). In the meantime, extensive macroalgal blooms and severe brown tide (*Aureococcus anophagefferens*) caused low water clarity and resulted in wide seagrass dieoffs, and severe infestations of noxious jellyfish in the Barnegat Bay-Little Egg Harbor Estuary (Kennish 2009).

3.3 Effect on Phytoplankton Community

Although it is well documented that anthropogenic nitrogen and phosphorus flux drive the proliferation of extensive phytoplankton blooms everywhere in the aquatic habitat (Brodie and Mitchell 2006; Dorgham 2011), they also cause change in the speciation of phytoplankton (Crosbie and Furnas 2001; Ismael and Dorgham 2003). Shifts of phytoplankton species to larger forms of diatoms and dinoflagellates with a contemporary increase of dissolved inorganic compounds of both nitrogen and phosphorus (Furnas et al. 2005) were most obviously documented in several tropical locations, such as Singapore (Gin et al. 2000), Japan (Tada et al. 2003), Curacao (Van Duyl et al. 2002), New Caledonia (Jacquet et al. 2006), Hawaii (Cox et al. 2006), and Moorea (Delesalle et al. 1993). In the Great Barrier Reef lagoon near Low Isles, eutrophication has occurred over the past 65 years, and caused a change from a system characterized by both centric and pennate diatoms to one that is now dominated by pennate diatoms and small flagellates (Bell and Elmetri 1995).

The variable nutrient requirement of different phytoplankton groups is one of the crucial factors that impact the community structure and the ratios between the different nutrients (N:P, Si:N and Si:P) and lead to a shift in phytoplankton community. The suitable ratio of silicon to nitrogen (Si:N) for diatoms growth is about 1 (Redfield et al. 1963; Dortch and Whitledge 1992); change of this ratio causes a pronounced drop in the growth rate of diatoms, and results in consequent change in the predominance of other algal groups that usually require small amounts of silicon (Conley et al. 1993). In the German Bight, the decline in the Si:N ratio to <0.1 during the period 1962–1984 caused the decrease of the abundance of diatoms and increase of flagellate/dinoflagellates (Radach et al. 1990), with the pronounced abundance of some toxic species or harmful blooms such as the flagellate *Phaeocystis* sp. which extended its seasonal duration blooms in the Wadden Sea (Richardson 1997). Numerical displacement was reported of diatoms with other different phytoplankton groups (Paerl 1997), particularly in diverse regions of the North Sea, which experienced decreasing Si:N and Si:P ratios (Riegman et al. 1992). In contrast, decreased Si:N with increasing nutrient fluxes of nitrate led to an increase in abundance of marine planktonic diatom *Pseudo-*

nitzschia in the northern Gulf of Mexico since the 1950s (Parsons et al. 2002) and in the Santa Barbara Channel, California (Anderson et al. 2006). The freshwater input to the Chesapeake Bay caused a continuous decline in diversity and a marked rise of centric/pennate ratios in most recent sediments (Cooper 1995).

The ratio between dissolved organic carbon and dissolved organic nitrogen (DOC:DON) appeared to play a role in the change of the species composition of phytoplankton community. Shifts in species composition have been recently reported in association with the change in DOC:DON (Anderson et al. 2002). Succession of heterotrophic and mixotrophic dinoflagellates as well as autotrophic microplankton (Ismael 2003) and different phytoplankton groups (Ismael and Dorgham 2003) were reported in eutrophic harbor of Alexandria on the southeastern Mediterranean, Egypt.

Shifts in phytoplankton communities in eutrophic areas lead to pronounced changes at higher trophic levels, while eutrophication inhibits the production of lipids by some fresh water diatoms that are essential for zooplankton sexual reproduction (Kilham et al. 1997), and retards the growth of certain species of phytoplankton that secrete heat-stable metabolites which enhance the spawning of green sea urchins and blue mussels (Starr et al. 1990).

3.4 Eutrophication and HABs

The eutrophication resultants are the HABs, which cause serious ecological problems in the aquatic ecosystems and detrimental injury to living organisms. HABs are one of the increasing frequent threats to aquatic ecosystems worldwide resulting from eutrophication (Rabalais et al. 2009). They can negatively affect the aquatic animals in localized areas as well as in the whole ecosystem (Graneli and Turner 2008) by activities such as clogging of fish gills (Graneli and Turner 2008), poisoning by toxins secretion (Kim et al. 2002), and causing localized anoxia (Anderson et al. 2002).

A more recent increase in harmful bloom events occurred in the southern hemisphere regions, particularly in the area under human stress, such as blooms of the toxic dinoflagellates *Alexandrium tamarense* and *Alexandrium catenella* in South African, Australian, Indian, and Thai coastal waters (Hallegraeff 1993). Meanwhile, certain systems in northern hemisphere showed pronounced symptoms of eutrophication, such as Baltic, North Sea, northern Adriatic, and western Mediterranean seas (Paerl 1997) and southeastern Mediterranean (Dorgham 2011).

Although several studies indicated no direct link between eutrophication and HABs in estuarine and coastal waters (Andrén 1999), others reported such linkages (e.g., Pan et al. 2001; Dorgham 2011), and numerous HABs were recorded in different eutrophic coastal areas worldwide, such as blooms of *Pfiesteria piscicida and Pfiesteria shumwayae* in the Albemarle-Pamlico and Chesapeake Bay (Marshall et al. 2006; Lewitus et al. 2008), the cyanobacterium *Microcystis aeruginosa* (Marshall et al. 2005), the dinoflagellate *Karena brevis* in both the coast of west Florida (Brand and Compton 2007), and the Gulf of Mexico (Walsh et al. 2006). The mid-Atlantic region has many HAB species, their frequency and abundance increasing with increased nutrient loading (Anderson et al. 2008). The mid -Atlantic region has many HAB species, their frequency and abundance increasing with increased nutrient loading.

In the brackish part of the Baltic Sea, excessive phosphorous loading caused the increase of the bloom of toxic cyanobacteria species, *Aphanizomenon flos-aquae* and *Nodularia spumigena* (Niemi 1979).

Several of the HABs associated with eutrophication cause human illness, similar to those reported in USA, including Narragansett Bay (Li and Smayda 2000), Florida Bay (Glibert et al. 2004), the Texas coast (Buskey et al. 2001), and San Francisco Bay (Lehman et al. 2005). In the northeastern USA, the harmful dinoflagellate *Alexandrium fundyense* causes Paralytic Shellfish poisoning (PSP) and impacts other food resources such as lobsters, fish, and marine mammals (Anderson et al. 2008), while the nonmotile pelagophyte *Aureococcus anophagefferens* was reported to cause destructive brown tide bloom in northeast and mid-Atlantic US estuaries for two decades (Gobler et al. 2005). In addition, numerous species were found to form harmful blooms in the mid-Atlantic, such as *Prorocentrum minimum*, *A. anophagefferens*, *Microcystis aeruginosa*, *Pfiesteria piscicida*, *P. shumwayae*, *Karlodinium veneficum*, *Heterosigma akashiwo*, *Chattonella subsalsa* and *Chattonella* cf. *vericulosa*, and *Fibrocapsa japonica* (Anderson et al. 2008). The dinoflagellate *Gymnodinium aureolumi* caused repeated fish kills in aquaculture systems in the Tunisian lagoons (Romdhane et al. 1998).

The harmful effect of algal blooms is not confined to the toxic species, but algal blooms of numerous nontoxic species can cause harm through their high biomass, forming foams or scums on the surface water, the depletion of oxygen as blooms decay, or the destruction of habitat for fish or shellfish by shading of submerged vegetation (Anderson et al. 2002).

Cyanobacteria that blooms as the most common harmful algae since the beginning of the second half of the twentieth century in numerous freshwater basins (Chorus and Bartram 1999) can cause wide varieties of nuisance or harm to the environment, such as thick hyperscum mats (Zohary and Roberts 1989), production of potent hepatotoxins and neurotoxins, causing livestock and wildlife death (Codd et al. 1997), and occasionally human death (Chorus and Bartram 1999).

The serious eutrophication during the 1960s and 1970s in the Seto Inland Sea in Japan led to a dramatic increase in red tides incidents by the Raphidophyceae, *Chattonella*

Table 3.1 Fishery loss owing to impact of harmful algal blooms (HABs) of some toxic algal species in different marine habitats

Species	Year	Area	Loss	Type of loss	Reference
Chattonellaantiqua	1972	Seto Inland Sea	Fish	US$ 60×10^6	Imai et al. 2006
Chattonellaantiqua	1979–2004	Seto Inland Sea	Fish	100×10^6 Yen	Imai et al. 2006
Heterocapsacircularisquama	1998	Seto Inland Sea	Oysters	3.9×10^9 Yen	Imai et al. 2006
Gonyaulaxpolygramma	1994	Seto Inland Sea	Fishery	80×10^6 Yen	Koizumi et al. 1996
C. polykrikoides	2000	Yatsushiro Sea	Fishery	4×10^9 Yen	Yoon 2001
C. polykrikoides	1995	Korean coastal waters	Fishery	76.4×10^9 won	Kim et al. 2002

Table 3.2 Water discoloration and finfish mortality events in different Greek waters owing to HABs

Toxic species	Year	Area	Type of loss	Reference
Alexandriumminutum				
Noctilucascintillans	2000–2004	Thermakos Gulf	Water discoloration	Nikolaidis et al. 2005
Chatonellaglobosa	2000–2004	Thermakos Gulf	Water discoloration	Nikolaidis et al. 2005
Dinophysis acuminate	2000–2004	Thermakos Gulf	Shellfish death	Ignatiades and Skretas 2010
C. globosa	2001–2003	Thermakos Gulf	Water discoloration	Ignatiades and Skretas 2010
Kareniabrevis	1977–1978	Saronikos Gulf	Fish kill	Ignatiades and Skretas 2010
Phaeocystispouchetii	1989, 1993	Saronikos Gulf	Water discoloration	Ignatiades and Skretas 2010
Phaeocystispouchetii	1999	Evoikos Gulf	Mucilage problems	Ignatiades and Skretas 2010
C. veruculosa	1999	Amvrakikos Gulf	Finfish mortality	Ignatiades and Skretas 2010

antiqua, *C. marina*, *C. ovata* and *Heterosigma akashiwo*, and the Dinophyceae *Karenia mikimotoi* and *Cochlodinium polykrikoides* (Imai et al. 2006).

The effect of HABs on living resources has been documented in several coastal and marine habitats, where different toxic species led to detrimental effect on the fishing resources and caused mass mortality of variable aquatic animals resulting in great economic loss, mainly in Japan (Table 3.1).

In addition, the Greek coastal waters were exposed to various algal blooms, mainly by toxic dinoflagellate species, which caused water discoloration, undesirable esthetic symptoms and anoxic harmful conditions to the ecosystem, and finfish mortality events (Table 3.2).

Furthermore, numerous events of toxic algal blooms have been frequently reported in recent years in different parts of the world in coastal waters by the Intergovernmental Oceanographic Commission of UNESCO (http://www.unesco.org/ioc/news/newslet/ htm). These events include toxic blooms of the diatom *Pseudonitzschia australis* in California coastal waters; *Pseudonitzschia pungens* in estuaries of Prince Edward Island, Canada; multiple species of dinoflagellates in Hong Kong and south China; brown tide species in Saldanha Bay and Langebaan Lagoon, South Africa; the dinoflagellates *Gymnodinium mikimotoi* in Wellington Harbor, New Zealand; *Alexandrium tamarensis* in Brazil, Uruguay, and Argentina; red tides along the Salalah coast of Oman; *Pyrodinium* in Acapulco, Mexico; *Alexandrium* spp. in Alexandria Harbor, Egypt; *Gymnodinium breve* in south Florida; *Gymnodinium catenata* along the Atlantic coast of Morocco; *Dinophysis* in Loch Long, Scotland; *Alexandrium minuta* in the Bay of Izmir, Turkey; *Dinophysis* along the northeast coast of Kamchatka, Russia; *Pyrodinium bahamens* in the Philippines; and *Gymnodinium nakasagiense* in southwestern India (Cloern 2001).

The HABs not only cause mortality of marine animals but they also impact different life activities of these animals, as they can negatively impact the growth and reproduction of invertebrates. For example, brown tides caused by the chrysophyte *Aureococcus anophagefferens* impaired reproduction of the copepod *Acartia tonsa* in Laguna Madre, USA (Cloern 2001), cyanobacteria blooms caused strong reduction in copepod egg production in the Baltic Sea (Sellner et al. 1996), blooms of the toxic dinoflagellate *Gymnodinium* cf. *nagasakiense* caused a marked drop in scallop standing crop (*Pecten maximus*) in the Bay of Brest (Cloern 2001). Furthermore, accumulation of organic matter derived from mass sedimentation of the diatoms *Rhizosolenia delicatula* and *Chaetoceros sociale* caused small depressions in its growth of scallop (Chauvaud et al. 2000), while some diatoms species excrete aldehydes which inhibit growth of some invertebrates such as copepods and urchin (Miralto et al. 1999).

3.4.1 Effect on Benthic Life

Eutrophication has been reported as an increasing ecological threat to benthic life in numerous coastal areas, mainly because of the resulting hypoxia and/or anoxia conditions with

devastating effects on the benthic macrofauna. In several parts of the Baltic Sea, the benthic fauna was pronouncedly affected by the anoxia conditions since the 1950s and 1960s as a result of increased organic enrichment, sometimes below 70 m depth, with a total loss of benthic macrofaunal biomass of 3 million tonnes (Karin et al. 2002).

Accumulations of attached and/or drift macroalgae in shallow waters cause changes in bed roughness and trapping of fine-grained sediments and negatively impact survival of invertebrate recruits, exclusion of some deposit-feeding and suspension feeding invertebrates such as amphipods and spionid polychaetes, and reduced abundance of invertebrate prey for fishes and shorebirds (Raffaelli et al. 1998). In tropical and subtropical waters, the enhanced macroalgal production led to the overgrowth and replacement of corals (Lapointe 1997) and caused a change in the populations of benthic invertebrates (Diaz and Rosenberg 1995).

The effect of eutrophication on the benthic communities appeared in animal-community responses to change in organic enrichment (Pearson and Rosenberg 1978), such as the increased benthic biomass in the Danish estuaries (Josefson and Rasmussen 2000), changes in species composition of macrozoobenthos in the Dutch Wadden Sea from 1970 to 1990 and in the Oslofjord and Skagerrak (Rosenberg et al. 1987), a sharp decrease in the macrozoobenthic biomass since the 1980s in the East China Sea (Wang 2006).

The hypoxia condition in bottom waters causes the escape of sensitive demersal fishes (cod, whiting) and other benthic fishes (dabs, flounder); mortality of bivalves, echinoderms and crustaceans; and extreme loss of benthic diversity (Gray 1992) which led to changes in the diet of bottom-feeding fishes as well as shift in dominance among demersal fish species in Kattegat (Pihl 1994).

The long-term eutrophication (1980–2000) caused dramatic changes in the Mondego estuary (Portugal), leading to a decline in seagrass beds and in species richness and replacement of herbivores by detritivores (Cardoso et al. 2004). Meanwhile, during (1968–1971 and 1993), in shallow coastal areas of the Baltic Sea, eutrophication caused significant change in the shoot density and biomass of the sea grass *Zostera marina*, associated with significant increase of total abundance and biomass of zoobenthos (Boström et al. 2002)

In the southern Kattegat, the effects of eutrophication resulted in the change of macrophytes above halocline from *Fucus* spp. to filamentous green algae and mortality of benthic macro fauna (mainly bivalves) in most years and seasons. Meanwhile, below the halocline, hypoxic conditions caused the disappearance of fish, immobilization and/or death of lobsters, and emergence of benthic infaunal species from the sediment (Baden et al. 1990).

Increased macroalgal biomass and decreased oxygen concentrations in the bottom waters led to mortalities of benthic animals and decreased fish catches in the Baltic, Swedish and Danish coastal areas in the Kattegat and the Belt Sea as well as in the Danish North Sea coast (Rosenberg 1985).

The hypoxia conditions induced by eutrophication inhibited growth of benthic animals, particularly sediment-dwelling invertebrates, such as the polychaete *Nereis (Hediste) diversicolor*, the bivalve *Abra alba* and the brittle star *Amphiura filiformis* (Hylland et al. 1996). In the lower York River, Chesapeake Bay, USA, extensive hypoxia caused mass mortalities of benthic organisms on the inner continental shelves of the New York Bight and the northern Gulf of Mexico off Louisiana and Texas (Boesch and Rabalais 1991). In addition to mass mortality of the benthos in the Bay of Somme, English Channel, anoxia conditions led to the disappearance of the common cockle *Cerastoderma edule* and proliferation of the polychaete *Pygospio elegans* as well as changes in the diet of the two main predators of the bivalve, the oystercatcher *Haematopus ostralegus*, and the common gull, *Larus canus* (Desprez et al. 1992).

In Korean coastal waters, low dissolved oxygen and organic enrichment caused defaunation during summer hypoxia, with the persistence of the polychaetes, *Sigambra tentaculata*, *Mesochaetopterus* sp., and *Lumbrineris longifolia* (Lim et al. 2006), while in the Aland Islands, northern Baltic Sea, long-term eutrophication caused a drastic change in abundance and biomass of the benthic communities and the appearance of a new polychaete species *Marenzelleria viridis* over the entire region, which became among the most dominant benthic assemblages (Perus and Bonsdorff 2004). Declined macroinvertebrate density and a more variable species composition under eutrophication were also reported in Peel–Harvey Estuary and the Indian Ocean, associated with proportionally less abundant crustaceans and high abundant Polychaetes (Wildsmith et al. 2009).

Excessive nutrient loading has led to the decline and disappearance of rooted vegetation that is critically important to the survival of animals such as certain zooplankton, finfish, and/or shellfish which graze on algae (Anderson et al. 2002). However, increase of algal growth/organic production rates led to changes in the benthic community structure, such as replacement of hermatypic corals with coralline algae, filamentous algae, macroalgae, and/or a variety of filter feeders (Bell et al. 2007), and increase of bioerosion in some forms (Hutchings et al. 2005).

Under the increase of drifting mats of annual algae in the Baltic Sea, benthic community reduced significantly in the species number and the dominance pattern, such as the significant reduction (>70%) of the spat settlement of the dominating bivalve *Macoma balthica*, complete disappearance of the dominating polychaetes *Pygospio elegans* and *Manayunkia aestuarina*, and great increase in numbers of the amphipod *Corophium volutator* (Bonsdorff 1992). Also, rocky shore communities became dominated by single spe-

cies of annual algae or filter feeders, and community diversity declined consistently by 24–46 % in the Northwest Atlantic and eutrophied sites in the Baltic Sea (Worm 2006).

Under hypoxic conditions owing to decomposing algal mat on shallow sandy bottoms in the northern Baltic Sea, the bivalve *Macoma balthica* emerged at the sediment surface, and exposed to epibenthic predators, such as the isopod *Saduria entomon,* the brown-shrimp *Crangon crungon* and the flounder *Platichthysflesus* (Norkko and Bonsdorff 2008). However, the intensive growth of periphytic algae caused an increase in the number of egg-carrying females of gammaridean *Gammarus locusta* as their egg reared on periphyton (Kraufvelin et al. 2006). On the other hand, eutrophication causes shifts in plant communities by qualitative changes in the dominance of perennial macroalgae and seagrasses toward the dominance of ephemeral macroalgae and pelagic microalgae (Borum 1996), which may lead to pronounced changes in habitat quality for animals such as the disappearance of the scallops when seagrasses were replaced by macroalgae (Kennish et al. 2007).

3.4.2 Effect on Trophic Linkage

Eutrophication plays a significant role in trophic linkage between pelagic and benthic communities in the coastal waters. In Lake Tahoe, zoobenthos obtained 27 % of their energy from phytoplankton sources before eutrophication, while after 43 years of eutrophication, they obtained 62 % from pelagic sources.

1. This led to a change in the feeding habit of higher consumers, such as the benthic fish (*Catostomus tahoensis*) which now derives ~21 % of its energy from pelagic primary production source (Chandra et al. 2005).
2. Intermediate link between the water column and demersal fishes could also be affected by eutrophication and will impact (as prey) on the demersal fish production.

In the Neuse River Estuary, North Carolina, the low oxygen level in bottom-water caused dramatic decrease (over 90 %) in abundance of the clam *Macoma balthica*, a key prey item for fishes and crabs, which resulted in a shift in croaker diet away from clams to less nutritional items such as plant and detrital material (Powers et al. 2005).

Eutrophication can indirectly affect the trophic linkage in the marine environment. Increasing turbidity with eutrophication in a Baltic inlet, led to a shift from a perch dominated community to a cyprinid dominated one, because perch growth was reduced in eutrophic areas, especially in the size range owing to change from foraging on zooplankton to benthic organisms (Sandstrom and Karas 2002). The growth rates of yellow perch in Lake Erie's declined sharply at the hypereutrophy conditions owing to food limitation related to a reduced size of their benthic prey (Hayward and Margraf 1987). In the Kattegat, the diets of five dominant bottom-feeding fish species, Atlantic cod (*Gadus morhua*), whiting (*Merlangius merlangus*), plaice (*Pleuronectes platessa*), dab (*Limanda limanda*), and American plaice (*Hippoglossoides platessoides*) showed a general long-term change owing to changes in species composition of benthic macrofauna, whereas several infaunal species increased in dietary importance during recent hypoxia, and reduction of epibenthic crustaceans was observed in the fish diet (Pihl 2011).

In shallow coastal areas along the Swedish west coast, a general proliferation of filamentous algae caused less successful foraging areas for cod and consequently led to considerable alterations in trophic relationships (Isaksson et al. 1994). The frequent mass mortality of the benthos under anoxia conditions in the Bay of Somme, France led to the disappearance of benthic bivalve *Cerastoderma edule* and the proliferation of the polychaete *Pygospio elegans* and consequently to apparent higher-up in the food chain through changes in the diet of the two main predators of the bivalve, the oystercatcher *Haematopus ostralegus* and the common gull *Larus canus* (Desprez et al. 1992).

3.4.3 Effect on Seagrasses

Eutrophication is one of the factors contributing to the decline of seagrass ecosystems worldwide (Richardson 2006). Severe shading and light attenuation caused by blooms of both macroalgae and phytoplankton hinder photosynthetic processes in benthic plants and sea grass habitats (Walker et al. 1999), that reached at some coastal areas > 70 % of the seagrass habitats (Lamote and Dunton 2006). Water turbidity also negatively effects the depth distribution of macroalgae (*Fucus vesiculosus*), while dense accumulations of macroalgae form thick canopies on seagrass beds and smother shellfish and other invertebrate fauna inhabiting the beds (McGlathery et al. 2007). Significant losses of seagrass beds associated with the algal bloom of the persistent brown tides have been reported in Laguna Madre (Cloern 2001), and an increase of epiphyte loads in some mid-Atlantic areas (Silberstein et al. 1986), which represents the major mechanism of seagrass die-off worldwide (Bricker et al. 1999).

High nutrients levels may lead to a disturbance in nitrogen and phosphorus metabolism in seagrass (Touchette and Burkholder 2000), and consequently cause a change in plant communities relative to their responses to the different nutrients, such as the toxicity of ammonium to the eelgrass *Zostera marina* (Van Katwijk et al. 1997). Strong inverse relationship was reported between eelgrass habitat and nitrogen concentration in the overlying water in Danish estuaries (Risk et al. 1995), and between the global declines of seagrasses and depletion of dissolved silicon (Herman et al. 1996).

The hypoxia conditions in the northern Barnegat Bay-Little Egg Harbor Estuary appeared to be associated with decreased biomass, density, and areal cover of the submerged aquatic vegetation from 2004 to 2006 (Kennish et al. 2008), with a degradation of about 50–87.8 % (Kennish et al. 2007).

In contrast to the degrading effect, eutrophication may play an enhancing role in the growth of seagrasses. A gradual increase in seagrass distribution was reported since the 1950s at Green Island owing to regional increase in anthropogenic nutrient (Udy et al. 1999), while along the north Queensland coast the tissue nutrient status of the seagrass *Halophila ovalis* has increased over a 20-year period with increasing fertilizer usage (Mellors et al. 2005).

Furthermore, eutrophication is a principal factor promoting massive accumulations of macroalgae worldwide, such as in Tunis and Venice Lagoons (Sfriso et al. 1993), Saint Brieuc Bay and other open coastal systems in France (Menesguen 1992), Waquoit Bay and other urbanized embayments in the northeastern USA (Valiela et al. 1997) and the Peel Harvey estuary in western Australia (McComb et al. 1981). In an intertidal area of the German North Sea coast, eutrophication was associated with pronounced increase in the macroalgae cover (Chlorophyta, Ulvaceae) in 1990–1992, sometimes to 30–60 % of the tidal flats (Kolbe et al. 1995).

3.4.4 Effect on Coral Reefs

Eutrophication exhibited variable effects on the corals, such as recruitment, diversity, collapse of coral reef community, trophic structures, mortality, bioerosion, associated communities, decrease in skeleton density, misshaped aragonite structure, and bioerosion. In the Whitsunday Islands, corals could recruit in eutrophic areas, near the mouths of rivers, but the recruits failed to survive (Cooper et al. 2007). Along the leeward coast, west of Barbados, the effects of eutrophication processes were directly and/or indirectly affecting the community structure of scleractinian coral assemblages (Tomascik and Sander 1987b), since eutrophication can restrict coral growth and reproduction and may cause virtual extinction of some species, particularly sensitive to eutrophication, such as *Acropora palmata* (Bell and Tomascik 1993), owing to higher mortality of juveniles on the eutrophic reefs than the less eutrophic reefs (Wittenberg and Hunte 1992). On the other hand, under nutrient enrichment from upwelling waters, juvenile scleractinian corals were outcompeted for space by opportunistic algae and tunicates, resulting in reduced survivorship (Birkeland 1977).

The diversity of hard coral species and algal cover was reduced in the region between Cardwell and Cape Flattery owing to increased effect of land-based effluents (DeVantier et al. 2006), as high nutrient levels may exhibit different impacts on coral communities (Fabricius 2007), such as collapse of coral reef community (Smith et al. 1981), bioerosion (Risk et al. 1995), altered biodiversity (van Woesik et al. 1999), reduced recruitment and modified trophic structures (Fabricius 2005).

The organic compounds released from nutrient-induced algal blooms promote microbial activity on coral surfaces and cause coral mortality (Smith 2006), while synergistic effect of both the dissolved organic matter and rates of bioerosion has a pronounced role in reef degradation (Kline et al. 2006). In Kaneohe Bay, Hawaii, intensive biological activities such as phytoplankton blooms associating eutrophication led to loss of live corals (Caperon et al. 1971) and increase of filter and deposit feeders such as tube worms and sponges (Kinsey and Devies 19) and increase in cryptofauna biomass (Brock and Smith 1983).

Essential shifts in the physicochemical and biological environment of coral reef ecosystems are usually associated with the eutrophication process (Tomascik and Sander 1987b) and cause environmental disturbance to coral reef (Hoegh-Guldberg et al. 2007) resulting in reductions in live coral cover, and concomitantly effects on the diversity and abundance of other reef-associated communities (Pratchett et al. 2008).

Nutrient enrichment causes the shift in species composition of the coral reef-associated community (Done 1992) as larger, slow-growing organisms, surviving in nutrient-poor waters are replaced by smaller, rapidly growing species in elevated nutrient concentrations (Birkeland 1988). In addition, the intensive algal growth overgrows and outcompetes corals for hard substratum and hinders coral growth (Larkum and Steven 1994). In the Gulf of Oman, large-scale HABs of the dinoflagellate *Cochlodinium polykrikoides* in October/November 2008 caused the complete loss of the branching corals, *Pocillopora* and *Acropora* spp., and substantial reductions in the abundance, richness, and trophic diversity of the associated coral reef fish communities (Bauman et al. 2010).

Since numerous coral reefs prefer to grow in nutrient-poor waters, eutrophication and siltation have severely stressed many fringing and offshore reefs (Brown 1997), particularly on long-term scale (Kramarsky-Winter et al. 2009), and caused physiological changes in growth and skeletal tensile strength, decrease of reproductive effort, and a reduced ability to withstand disease (Loya 2007). On the other hand, high levels of nutrients demonstrate a pronounced effect on the coral community (Birkeland 1988) reflected on a number of biochemical parameters (Larkum and Steven 1994) such as changes in metabolism, density of the zooxanthellae and chlorophyll concentration per cell (Muscatine et al 1989), decrease in skeleton density, and misshaped aragonite structure (Strambler et al. 1991). In addition, high concentration of phosphates can inhibit coral reef calcification by more than 50 % (Kinsey and Davies 1979) and suppress benthic

coralline algae, the important coral reef builders (Björk et al. 1995).

Increasing sediment load caused by eutrophication can cause pronounced changes in the environmental characteristics of coral reef ecosystems (Rogers 1990), and affect growth rates, reproduction, and community structure of scleractinian corals (Tomascik and Sander 1987b). In addition, eutrophication may negatively effect on coral reefs through some trophic relations between various flora and fauna. In some regions of the Great Barrier Reef lagoon, eutrophication-induced algal overgrowth promoted outbreaks of the crown of thorns starfish, the active predator of coral recruitment (Fabricius et al. 2010). Sedimentation by algal growth decreased the available light and caused a decline in the hermatypic reef corals (Tomascik and Sander 1987a; Rogers 1990), while macroalgal bloom can inhibit reef coral growth and recruitment (Smith et al. 1981), leading to loss of coral cover in eutrophic tropical hard-bottom communities (Lapointe and Clark 1992)

3.4.5 Effect on Zooplankton

The effects of increasing eutrophication on the crustacean zooplankton composition have been reported in many marine habitats worldwide. These effects appeared in species diversity, community structure, size, reproduction rate, and feeding habits. Owing to its wide array of diversity zooplankton community demonstrates variable and sometimes contradictory trends in responses to eutrophication (Hulot et al. 2000) whereas intensive eutrophication may lead to a significant increase in the number of zooplankton species, disappearance of some species, and marked increase of abundance (Ostoijc 2000). In addition, significant changes were reported in the species diversity indices (Kozuharov et al. 2007) in dominant species and alteration of zooplankton species diversity and succession (Park and Marshall 2000). However, eutrophication may cause a decline in species richness and in the abundance of zooplankton (Sendacz et al. 2006) and an increase of large-sized phytoplankton forms (Breitburg et al. 1999), which provide better feeding conditions for the copepods (Hansen et al. 2000)

The variation in the loads of dissolved inorganic nitrogen (DIN) and inorganic phosphorus appeared to have a role in the changes of zooplanktoin community structure. The total mesozooplankton biomass as well as copepod and cladoceran biomass decreased with DIN, while both groups increased with the dissolved inorganics phosphorous (DIP) load (Zervoudaki et al. 2009). Opposite correlations were observed between zooplankton abundance and DIN (decrease) and DIP (increase) in the highly eutrophic tributaries of Chesapeake Bay (Park and Marshall 2000). However, protozooplankton (ciliates and heterotrophic dinoflagellates) biomass did not show any response to the enhanced nutrients (Zervoudaki et al. 2009).

In the Belgian Coastal Zone and the Southern Bight of the North Sea, the predominant colonial haptophyte *Phaeocystis globosa* (Muylaert et al. 2006) negatively impacted the dynamics and life cycles of zooplankton (Lancelot and Rousseau 1994, Lancelot et al. 2002) such as the nauplii and copepodites I–V of the copepod *Temora longicornis* (Daro et al. 2006), which may be attributed to the thick gelatinous sheet surrounding the *Phaeocystis* colonies and/or its poor nutritional value (Tang et al. 2002).

Eutrophication may impact zooplankton size (Matsumura-Tundisi 1999) as reported in the Pampulha reservoir, Brazil, where zooplankton suffered extensive qualitative and quantitative changes, particularly in size and biomass of certain zooplankton groups owing to the replacement of small cladocerans such as *Bosmina* and *Ceriodaphnia* by another relatively large cladoceran, *Moina micrura* (Pinto-Coelho et al. 2005). A strong relationship between total phosphorus and particulate organic carbon may be responsible for such variations, owing to the relative importance of the detrital food chain for the planktonic community in the Pampulha reservoir (Pinto-Coelho et al. 2005) which in turn may affect the balance between primary and secondary production (Araújo Araujo and Pinto-Coelho 1998). A significant linear regression observed between biomass of zooplankton and/or certain groups (e.g., cyclopoids) and total phosphorus suggests that the response of zooplankton to eutrophication achieved through the intensive growth of one of the major groups (Pinto-Coelho et al. 2005). However, no similar relationship reported between phosphorous and other crustacean zooplankton groups such as cladocerans and calanoids eutrophic waters (Pinto-Coelho et al. 2005) may be owing to the disappearance of the dominant zooplankters, like *Daphnia* (Pinto-Coelho et al. 2003) or disappearance of calanoids from these waters (Sendacz 1984).

The impact of eutrophication on the structure of zooplankton community is also related to the effect of other trophic levels, such as primary producers and fishes. For example, intensive growth of the macrophyte water hyacinth (*Eichhornia crassipes*) in eutrophic lake is accompanied with harmful mosquito propagation, the removal of which requires intensive removal of the hyacinth (Pinto-Coelho et al. 2005). This in turn causes ammonium decrease, nitrate increase, and a pronounced change in zooplankton community structure, such as the disappearance of the calanoid *Scolodiaptomus corderoi*, and the smaller cladocerans *Bosmina* and *Ceriodaphnia* (Pinto-Coelho and Araújo 1997). In addition, the macrophyte removal may enhance some bacterial bloom, such as the cyanobacteria *Microcystis* spp., which has a crucial role in the temporal patterns of major biochemical properties of the seston (Boechat 2000) and play a key role in the overall metabolism of phytoplankton, seston, and

zooplankton (Pinto-Coelho et al. 2005). In eutrophic environments with the recurrence of cyanobacterial blooms, zooplanktonic structure tends to be composed mainly of small-size organisms (Matsumura-Tundisi and Tundisi 2005) being efficient consumers of detritus and bacteria (Pace 1986) and cyanobacteria (Work and Havens 2003).

Top-down forces may affect the response of zooplankton to eutrophication (Hulot et al. 2000). In Pampulha reservoir, the size of cladoceran crusracea was less affected by piscivorous predation than what occurred owing to eutrophication, while biomass of nauplii and young copepodides of cyclopoid copepods increased with increasing fish predation and eutrophication (Pinto-Coelho et al. 2005). On the other hand increased zooplankton abundance from 1960s to 1980s in Lake Biwa was attributed to bottom-up effects driven by eutrophication (Tsugeki et al. 2003). The total zooplankton abundance showed a significant positive correlation with total phosphorus but the phytoplankton biomass showed a bottom-up control (Hsieh et al. 2011), which directly affects the fish propagation (Nakazawa et al. 2010).

Change in species composition and species replacement was among the resultant effects of eutrophication on zooplankton community. A bloom of the dinoflagellate *Ceratium hirundinella* in Albert Falls Dam caused the effective replacement of *Moina* by *Bosmina*, substantial reductions in *Daphnia* and *Ceriodaphnia*, and smaller but definite increases in abundance of calanoid copepods, as well as cyclopoid copepods (Hart and Wragg 2009). Such conditions lead to change in the ratio of cladoceran/calanoid and of cyclopoid/calanoid (Hsieh et al. 2011) as the increasing lake trophic status will favor cyclopoid over calanoid copepods and cladocerans over calanoids (Straile and Geller 1998). This was clearly shown in Lake Constance, on the Rhine at the northern foot of the Alps, during the 1950s and early 1960s, when the increase in crustacean biomass was accompanied by the dominance of *Cyclops vicinus* and *Daphnia galeata*, the extinction of *Heterocope borealis* and *Diaphanosoma brachyurum*, and increased biomass of all species which did not become extinct during eutrophication, causing a shift from a copepod-dominated lake to a cladoceran-dominated lake (Straile and Geller 1998). On the other hand, long-term records demonstrated the predominance of cyclopoids than calanoids within the copepods in eutrophic basins (Rognerud and Kjellberg 1984).

Eutrophication plays a crucial role in the change of zooplankton community structure (Karabin et al. 1997); the dominance shifts from macrozooplankton to microzooplankton with increasing trophic state, whereas the microzooplankton can constitute the major part of the total zooplankton biomass in eutrophic condition (Park and Marshall 1997). Tintinnids, copepod nauplii, and mesozooplankton significantly decreased with the increase of eutrophication (Park and Marshall 1997), while rotifers dominated the total zooplankton biomass in highly eutrophied waters (Zhao et al. 2007)

The effect of eutrophication on zooplankton community is also related to their taxonomy or feeding types, whereas herbivorous zooplankton (including rotifers and cladoceras) showed a positive response to phytoplankton biomass, while carnivorous and omnivorous zooplankton did not show a clear response to changes in trophic status (Hsieh et al. 2011). This pattern was observed in the Varna Lakes—Varna Bay with a gradient of eutrophication level, whereas Varna Bay was scaled as highly eutrophicated zooplankton abundance sustained the lowest value in Varna Bay compared to the Lakes, with the dominance of rotifers in both areas (Stefanova et al. 2007).

3.4.6 Effect on Fish

Mortality associated with the HABs is the most likely factor causing changes in fish community structure. During widely distributed scale (> 500 km^2) of the HABs, dead fishes and fish die-offs were reported elsewhere in the region (Richlen et al. 2010). Similar mass mortalities of fish communities have been associated with HABs events in both temperate (Landsberg 2002) and tropical environments (Smith 1975; Guzman et al. 1990). Rapid declines and changes in structure of coral reef assemblages were recorded within the Indian Ocean as a result of HABs (Bauman et al. 2010)

3.4.7 Effect on Foraminifera

Benthic foraminiferans have been widely used as indicators of eutrophication in coastal marine ecosystems (McGann et al. 2003). Off Southern California, eutrophication caused low species diversity and high population densities of the benthic foraminifera (Bandy et al. 1965), while in Long Island Sound (North-west Atlantic), the foraminiferan *Ammonia beccarii* dominated at nitrogen-rich effluent discharge (Thomas et al. 2000). In natural nutrient enrichment, Man O'War Cay (Belize), low species diversity of epiphytic foraminiferal communities was reported with the dominance of the encrusting, dendritic species *Cornuspiramia antillarum* living on the seagrass *Thalasssia testudinum* (Richardson 2006). A marked transition of foraminiferal patterns was recorded owing to the long-term development of hypoxia in front of the Po delta (northern Adriatic Sea) (Barmawidjaja et al. 1995).

In coral reef ecosystems, dramatic changes in the benthic foraminiferal communities could sometime occur during eutrophication, since the dominance of smaller opportunistic species led to a decline of larger endosymbiont-bearing taxa (Hallock et al. 2003). Progressive increase in the abundance

of the hypoxia-tolerant foraminiferan *Fursenkoina* sp. since the 1950s and disappearance of the more sensitive *Quinqueloculina* sp. in the 1870s in sediments of the Mississippi River Bight indicates the oxygen depletion (Rabalais et al. 1996).

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The Economics of Eutrophication

4

Eirik Romstad

Abstract

This chapter focuses on how economists deal with nonpoint source pollution where individual farm field emissions are not observed. This causes problems for the standard emissions marginal abatement cost framework used in environmental economics as it renders emission-oriented policy instruments not applicable. The advantages and disadvantages of the three main approaches of dealing with this issue—procedural regulations, input regulations, and regulations formulated to solve the information asymmetry issues—are briefly summarized. Finally, a brief overview on computable economic modeling is given.

Keywords

Bodeled emissions · Environmental damages · Eutrophication · Modeling · Nonpoint source pollution

4.1 Introduction

This chapter is bit special in a book on eutrophication with such a strong natural science orientation as it involves another science: economics. Therefore, parts of this chapter deal with some central economic concepts that will make it easier for natural scientists and economists to communicate with each other. The economic analyses presented in this chapter are limited to how to implement physical measures that emerge from the natural scientific analyses. Physical measures commonly entail some agricultural practice—like reduced fertilization and the planting of catch crops—that are expected to reduce eutrophication. If these physical measures were the most profitable, they would already have been implemented. In brief, reducing nutrient and pesticide leakages is costly for farmers, implying that many farmers resist or are opposed to undertaking these changes.

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This is where economic analysis comes in. It seeks to devise some policy instruments that make the desired changes in their agricultural practices from a eutrophication perspective the most profitable. Adoption of the desired practices is obviously straightforward if the desired practices coincide with the most profitable practices. Paying farmers to adopt desired practice is therefore one way of resolving the discrepancy between what is most desirable from an environmental perspective and what is most profitable for farmers. There are several problems with payments to reduce pollution. First, if agriculture were entitled to such payments, we would quickly see other polluting industries demand similar payments. That could quickly be quite costly for taxpayers. Second, paying someone not to do bad, i.e., pollute, comes at odds with widespread notions of fairness going back to kindergarten—those who make a mess are responsible for cleaning it up. Third, such payments may attract other firms into polluting sectors, which would further increase the strain on public funds.

A more realistic approach to reduce the differences in profits between the desired and current practices is to introduce taxes on pollution. Unfortunately, nonpoint source

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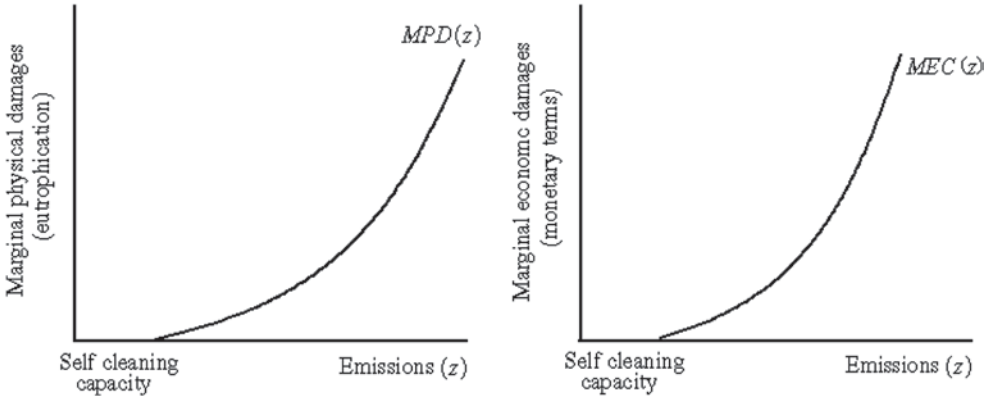

Fig. 4.1 Monotonic transformation of marginal physical damages MPD(z) into marginal economic costs MEC(z)

emissions from agriculture are not readily observable. That makes it difficult to introduce emission taxes (or subsidies to reduce emissions). There are, however, several other policy instruments available for reducing emissions that are not readily observable:

1. Command-and-control (CAC) regulations, i.e., the regulatory authorities by law require polluters to undertake certain actions that have been found to reduce emissions or improve the environmental quality of the recipient of the pollution.
2. Procedural regulations, often in the form of taxes on undesirable practices or payments (subsidies), for desirable practices.
3. Input taxes (or subsidies), i.e., input uses that are strongly linked to emissions become more expensive, which in turn lead to reduced use of the polluting input. Pesticide taxes are one example of such a tax.
4. Ambient regulations, i.e., those polluters are issued a tax if the environmental quality falls below a certain level, or are paid if environmental quality improves. Here, it should be noted that while nonpoint source emissions are difficult to observe, the resulting impacts on recipients may be readily observed.

Before proceeding with a discussion of these four main types of regulatory instruments, we need to have some notions about what is meant by environmental damages, optimal policies, and cost effectiveness. Briefly, optimality entails comparing the (expected) costs and (expected) benefits of policies to avoid levying too strict policies if perceived benefits are small compared to costs, or more commonly, to sharpen policies if costs are small compared to perceived benefits.

The structure of this chapter is as follows. First, I briefly discuss the linkages between physical damages and the economic concepts of environmental damages before cost effectiveness and optimality are addressed. Then, I frame nonpoint source pollution in an economic context with particular emphasis on asymmetric information. The following sections deal with the three types of economic instruments applied to nonpoint source pollution. Next, I present a brief overview of some computable (economic) models of nonpoint source pollution.

4.2 Environmental Damages

Economic analysis is not limited to policy instruments. Assessing the costs to society from pollution is another important branch of economic research. The intersection between the marginal abatement costs, i.e., the costs of reducing pollution, and the marginal benefits from pollution reductions, marks the optimal emission level from an economic angle. Estimates for society's marginal willingness-to-pay for pollution reductions can be obtained in many different ways. For a natural science readership, the least controversial way to get such estimates would most likely be to look at the physical damages caused by pollution and assess some monetary value to these damages. Usually, physical damages increase with higher pollution levels. This implies that the damages in economic terms would follow the same pattern. Commonly, economists operate with damage in economic terms as a monotonic transformation of the physical damages. This perspective does not preclude allowing for threshold impacts or discontinuities in the physical damage curve—an everywhere nondecreasing marginal physical damage curve as a function of emissions, $MPD(z)$, results in an everywhere nondecreasing marginal economic damage curve, $MEC(z)$. Figure 4.1 demonstrates this.

The presentation in Fig. 4.1 usually comes about from modeling physical damages or asking experts on the linkages between emissions and damages. Economists also have another approach of obtaining marginal economic costs denoted nonmarket valuation. These approaches can broadly be categorized into:

- *Revealed preference methods*: Where one deduces how people value various environmental goods and services based upon the choices they make (see Boxall et al. 1996 or Brown and Mendelsohn 1984 for an overview and Randall 1994 for a critical discussion).

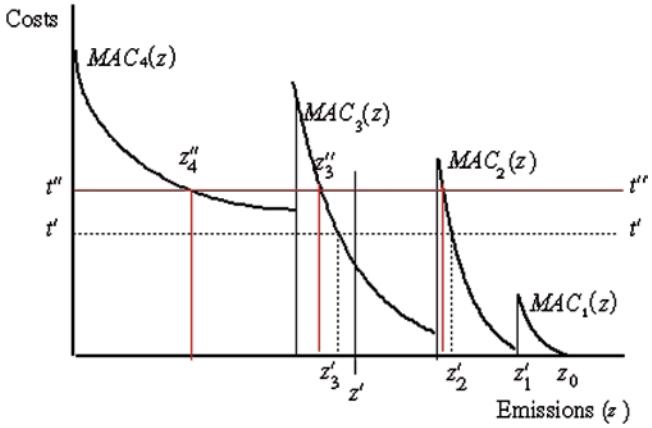

Fig. 4.2 Cost-effective allocation of emissions reductions

- *Stated preference methods*: Where people are asked about their willingness-to-pay for the environmental good or service in question (see Hanemann 1994 for an overview, and Diamond and Hausmann 1994 for a critical discussion).

Needless to say, the valuation estimates from such methods may differ from the estimates obtained from modeling exercises or expert assessments. The main point here is that in economics we would like to be able to compare the expected benefits of environmental improvements with the costs of obtaining these improvements.

4.3 Cost Effectiveness and Optimality

Cost effectiveness and optimality are key issues in environmental economics. A basic understanding of these concepts is necessary to understand how economists reason on pollution issues in general and eutrophication in particular. Cost effectiveness of an environmental policy is basically the least cost way of reaching a certain environmental target, for example, that emissions of nitrates to a receptor is not to exceed a certain level for a given time period. If faced with an emission constraint, it is quite obvious that economic agents (here polluters) would seek out the least cost way of not exceeding this constraint. A single polluter would hence implement the cheapest measure first, then the second cheapest measure, and so forth until his or her emissions are just at or below the permitted level. It is important to note that single measures may not be uniformly cheapest—as a measure is undertaken at increasing degrees; the costs associated with single measures tend to increase. Hence, the polluter would be looking at the combination of measures that yield the least cost way of meeting the emission constraint.

To see this more clearly, consider a polluter who has four ways of reducing his or her emissions of a pollutant from the current level z_0 to z'. The marginal abatement costs of these four measures are depicted in Fig. 4.2.

The horizontally dotted line, t', marks a distribution of emissions reductions between measures two and three that together with all measures one meets the emissions constraint, i.e., $z'=z'_1+z'_2+z'_3$. This distribution of emissions reductions is effective because:

- $MAC_1(z'_1)$ is below the horizontally dotted line of measure one.
- $MAC_2(z'_2)=MAC_3(z'_3)$, which implies there are no cost savings from redistributing abatement efforts between these two measures.
- None of measure four because its marginal abatement costs lie everywhere above the dotted line.

Now, suppose that measure one was unavailable. Then, to reach the overall emission target of z', one needs to do more of measures two and three. A cost-effective distribution under this new condition entails raising the line t'. To make the graph clearer, consider a raise of t' to t'' (this will produce a lower emission level than z'), so that the new allocations $z''_2>z'_2$ and $z''_3>z'_3$. Note that the new line t'' also makes measure four also enter the cost-effective solution with the amount z''_4 because $MAC_4(z''_4)=MAC_2(z''_2)=MAC_3(z''_3)=t''$. This also points to the general condition for cost effectiveness: that *the marginal abatement costs for all measures included in the cost-effective solution must have equal marginal abatement cost evaluated at the chosen emissions for each measure*. This is called the *equimarginal principle*.

One may think of the horizontal lines t' and t'' as taxes on emissions. A central theme in environmental economics is that polluter i abates until his or her marginal abatement cost evaluated at the chosen emission level, z' i, equals the emission tax rate, i.e., $t'=MAC_i(z'_i)$. As this holds for any agent, we can extend the *equimarginal principle* to multiple polluters.

It now follows that if polluters have different marginal abatement costs, equal emissions reductions does not constitute a *cost-effective allocation of emissions reductions across agents*. To see this, consider two agents who together have to reduce their emissions by a certain amount. One way of depicting this is in a bathtub diagram as shown in Fig. 4.3.

Figure 4.3 depicts two situations. First, it shows that if both polluters emit the same amount, i.e., $z'_A=z'_B$, this is not a cost-effective solution as $MAC_A(z'_A)$ is not equal to $MAC_B(z'_B)$. Second, if they *redistribute* emissions so that their marginal abatement costs are equal, i.e., $MAC_A(z''_A)=MAC_B(z''_B)=t''$, there are cost savings equal to the shaded triangle.

It should also be noted that regulators rarely know marginal abatement cost functions of individual polluters. Under such settings, it would be virtually impossible for the regulator to assign individual emission quotas to polluters that would implement the cost-effective solution illustrated in

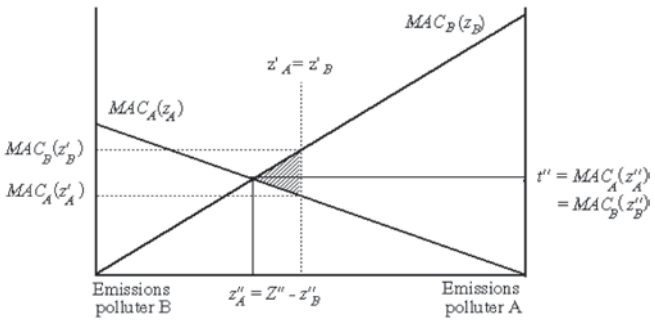

Fig. 4.3 Equal emissions are not cost-effective when marginal abatement costs differ across polluters

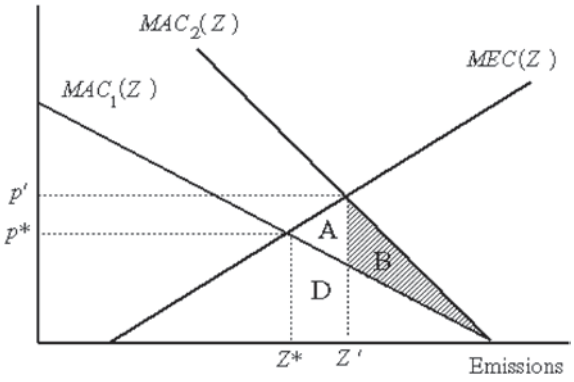

Fig. 4.4 Low-cost policies yield welfare gains and improve environmental performance

Fig. 4.3. Suppose instead that the regulator issues an emission tax like t''. Then, it is in polluter i's own interest to adjust emissions so that the cost-effective solution $t'' = MAC_i(z''_i)$. This is one reason why economists are skeptical toward CAC regulations, and instead prefer emission taxes, subsidies to reduce emissions, or tradable emission quotas. Under tradable emission permits, polluters with high marginal abatement costs buy emission right from polluters with low abatement costs until the emission quota price equals each polluter's marginal abatement costs.

Now, we are in a situation where we can proceed and discuss economic optimality. An allocation, Z^*, is optimal when the aggregate marginal abatement cost, $MAC(Z^*)$, equals marginal economic costs, $MEC(Z^*)$, where Z^* is the sum of individual polluter emissions.

The reason I emphasize these issues is that if we do not have cost efficiency, i.e., the equimarginal principle is met, the resulting aggregate marginal abatement costs will be higher than necessary. This has profound implications for the resulting aggregate emission level, and hence also for the environmental performance of an economy. Figure 4.4 illustrates these points.

Suppose the cheaper policy depicted by $MAC_1(Z)$ is chosen. Then, the emission level where marginal economic costs, MEC(Z) crosses the marginal abatement cost curve occurs at the emission level, Z^*. Compare that with a situation where the more costly policy, depicted by $MAC_2(Z)$ is chosen. This gives the perceived optimal emission level Z' which is higher than Z^*. Hence, environmental damages are higher and there is a welfare loss to society given by the shaded areas A and B. The figure therefore illustrates the importance of choosing low-cost policies and helps explain economists' "obsession" with low cost.

Economic optimality is also closely linked to the *net benefits* of policies, i.e., the environmental benefits justify the costs obtaining these benefits. When economic optimality is reached, net benefits are maximized. To see this, consider areas A and D, where the sum of A and D is the increase in environmental benefits while area D is the added cost from lowering emissions from Z' to Z^*. Hence, net benefits from the low-cost policies always exceed the additional costs. In addition, there is the extra cost savings moving from the high- to the low-cost policy illustrated by area B.

A final word of caution: while the low-cost policy is cheaper than the high-cost policy for the same emission level, Z', total costs of the low-cost policy may exceed those of the high-cost policy as emissions are further reduced under the low-cost policy. Whether this takes place or not depends on the size of the cost savings of the low-cost policy for reducing emissions to Z' (area B) relative to the additional costs of further reductions in emissions from Z' to Z^* (area D).

4.4 Nonpoint Source Pollution in an Economic Context

Unfortunately, nonpoint source emissions do not fit the standard economic framework of controlling emissions because it is technically difficult and costly to measure emissions from individual farm fields. Such measurement costs, frequently termed *transaction costs*, are to be included in the calculation of the social costs of abatement. This increases the costs of emission-based policies for nonpoint source emissions, and has led economists to consider other regulatory approaches that can replace emission-based policies: (1) *procedural regulations*, where farmers are instructed or induced to adopt certain practices and (2) *input-based regulations*, where the focus is on reducing use of inputs perceived to contribute to unwanted emissions. In his *optimal point of instrument application* (OPIA) framework, Vatn (2005) groups the desirability of various regulatory approaches according to their transaction costs and degree of emission homogeneity. This is illustrated in Fig. 4.5.

The dividing lines between these three types of regulation should be seen as indications, not absolutes. Despite this, the main issue in the figure—emissions regulations only fit a small spectrum of problems—remain. For economists, this is quite troublesome. Compared to input or procedural

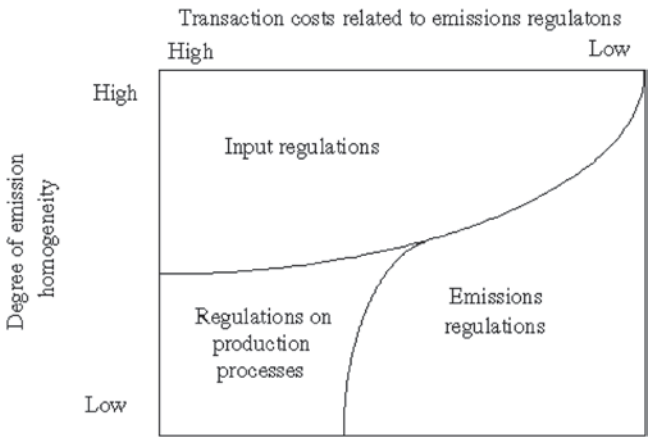

Fig. 4.5 Optimal point of instrument application given different degrees of emission homogeneity and transaction costs. (After Vatn 2005, p. 389)

regulations, emissions regulations have several desirable features that broadly can be summarized as follows: the focus is on the problem, which makes the regulatory framework more transparent, tractable, and traceable (Batie 2008).

As a result, economists have been searching ways to make emissions regulations applicable even in settings where transaction costs—in the nonpoint source emission setting, the costs of measuring emissions—are high. This gives rise to a third type of regulatory approach: regulations that seek to solve the problem of unobservable emissions from individual farm fields or properties. The latter class of regulations does not suffer from some of the problems associated with procedural or input-based regulations, but entails more complicated economic modeling where game theory (Gibbons 1997) and "truthtelling" (Holmstrom 1979) are key elements. I will return to these three classes of regulatory approaches.

The perceived environmental damages from emissions are the major reason why pollution control policies are implemented. Mean emission is the most frequent statistic reported for most pollutants. However, the distribution of emissions may also matter for environmental damages (Braden and Segerson 1993). For example, peak loads of nutrients into a stream may periodically deter water quality to the point that fish species are wiped out even if they are well adapted to the average emission levels. From a policy perspective, this adds complexity—a policy instrument that performs well when it comes to reducing mean emissions, may still lead to insufficient control of the variability in emission levels. As such, controlling mean emissions and their variability can be seen as two separate objectives, which leads us to the *Tinbergen* (1950) *principle*: In situations where there are multiple objectives and problems, at least one policy instrument should be used to alleviate each threat and pursue each objective.

The implications of the *Tinbergen principle* are profound: if separate instruments are used for each link between a threat and an objective, then it is simpler to readjust the policy mix as circumstances change. Climate change and economic recession are recent examples of such changes. For eutrophication issues, it is rather straightforward to see the importance of variability in climate and growing conditions.

4.5 Procedural Regulations

Procedural regulations are widely used to control nonpoint source emissions. Examples of such regulations include restrictions on how and when to spread manure, no-till or reduced tillage, or planting of buffer strips and vegetation zones. These three examples represent the main groups of procedural regulations. Each of these three groups will be discussed after I have addressed another issue—how to implement such regulations.

There are basically two ways of implementing procedural regulations: requiring farmers or subsidizing farmers to adopt the practice in question. Requiring certain practices sorts under CAC regulations. The main disadvantage of CAC regulations is that they could entail substantial cost for some producers. Hence, cost effectiveness is unlikely to take place. Still, many procedural regulations are implemented using CAC, in particular, on timing decisions like it is illegal to spread manure after a certain date in fall.

Subsidies to induce desired practices do not suffer from the same "stiffness" as CAC regulations. The reason for this is that farmers are allowed to choose between accepting the payment and adopt the desired practice **or** decline the payment and continue using their current practices. Any expected profit maximizing farmer will only choose to adopt the desired practice if the payment exceeds the expected loss in profits from adoption. Farmers with high adoption costs are therefore more likely to opt out of the scheme, while those with low adoption costs are more likely to opt in. The costs of adopting a new practice are likely to decline over time for two reasons. First, because it takes time for farmers to master the new practice. Second, because it takes time for producers of equipment to develop new machines suited for the new market created by the subsidy. A natural policy response to these time dimensions is to offer rather high payments in the early phase of implementing a procedural regulation and to reduce payments over time (to reduce the strain of the program on public funds). For example, when Norway implemented its reduced tillage program in grain production, it pursued such a strategy in the mid-1990s.

4.5.1 Timing Procedures

The time of manure application greatly influenced nitrate leaching (Van Es et al. 2006) and phosphorus leaching

(Van Es et al. 2004). At the first glance, such findings would lend support to applying CAC regulations for many timing decision. However, there is also substantial variability on phosphorus leaching owing to soil type, which implies that the environmental benefits from a time ban on manure spreading could vary. Hence, timing restrictions could also be subject to soil type. This would reduce the variability in environmental benefits and hence, also make such timing restrictions less costly.

The disadvantage of introducing a soil type adjustment to a time ban is that the costs of administering the regulation would increase as reports about manure spreading outside the spreading time window needs to be checked—does spreading take place on a soil type exempt from the ban or not?

To some extent, one may claim that some of the timing issues should sort themselves out. The main reason for this (bold) claim is that the application of manure or fertilizers in banned time periods contributes little to plant growth. Consequently, valuable nutrients are wasted. A caveat in this connection relates to manure treatment—where insufficient manure storage may still make it profitable for farmers to spread manure in periods where impacts on plant growth are limited and leaching higher. Under such settings, the problem is insufficient storage and directing regulations toward this is a more direct approach than timing restrictions. A modeling study by Vatn et al. (1997) shows that requiring sufficient manure storage reduces problems of manure spreading in unsuitable time periods in Norway, but at substantial costs to farmers who either have to expand their storage or reduce their number of livestock.

4.5.2 Production Method Procedures

The second group of procedural regulations—mandating certain production methods—is well illustrated by tillage requirements. Unlike timing procedures, the possibilities of using incentive-based (IB) regulations like subsidies appear far greater for this type of problems. As mentioned previously, the use of such payments allows farmers greater flexibility in their production decisions and hence also lower costs. An additional benefit of IB regulations is that payments can be adjusted over time as farmers gain experience or new and improved technologies become available.

Major drawbacks with subsidies are that they strain public funds and that they are inconsistent with widely held notions about fairness—farmers are paid to reduce their emissions while in other sectors of the economy, polluters pay unless they clean up. Cross-compliance resolves some of the funding and fairness issues. The basic idea of cross-compliance is that farmers who do not adopt desired practices or continue with undesired farming methods lose some of their other farm payments. Since the mid-1990s and until recently, cross-compliance has been an important part of the common agricultural policy of the EU. Trade issues and allegations under the WTO agreement about unjustified farm supports were important drivers for the EU adoption of cross-compliance.

Latacz-Lohmann and Hodge (2003) review the performance of the EU cross-compliance policy. They found that while better than subsidies on fairness and strain on public funds, cross-compliance policies had poor spatial targeting and suffered from a lack of clarity between environmental and income support objectives. In an early simulation study on erosion control measures, Ervin et al. (1984) reached many of the conclusions—cross-compliance policies are not well targeted and there were substantial distributive concerns as large farm operations benefited more than smaller operations. Although appealing at first sight, there are therefore many troublesome features of cross-compliance policies. In the revised common agricultural policy, the EU is therefore reducing its emphasis on cross-compliance.

It should also be noted that there has been substantial technological progress in the last 10--15 years, which has made reduced tillage as profitable as conventional tillage, in particular, for larger farm operations. The emergence of agricultural entrepreneurs has made many of these technological benefits available even for smaller farm operations.

4.5.3 Offsetting Procedures

Offsetting procedures like vegetation zones, buffer strips, and restoration of wetlands have gained increased attention. They can be implemented using CAC or IB regulations. In the IB variant, farmers are offered payments equal to the forfeited crop value of using land for offsets. On the eutrophication side, all these measures perform well in reducing nutrient leaching under stochastic weather events, serving as an end-of-pipe fix, and they are reasonably low cost (Byström et al. 2000). Additional benefits from such land use policies include biodiversity and the scenic value of landscapes (Gren et al. 1994), which partly deals with arguments that such offsets distort trade in an unfair manner. Land use policies have gained increased attention for controlling nutrient leakages (Hodge 2001).

4.5.4 Input Factor-Oriented Regulations

Input factor regulations come in two variants, CAC and IB. The IB form of input factor regulations are in the form of taxes on inputs that are perceived to contribute to nutrient leaching. Such taxes entail multiple benefits:

- They promote more efficient use of the taxed input and their close substitutes (like manure in the case of nitrogen fertilizer taxes). This increases their net benefits.

- They are well suited when emissions are heterogeneous, cf. Vatn's (2005) OPIA framework.
- They are cheap to administer as their transaction costs are close to zero.
- They produce tax revenues to the government instead of increasing the strain on government funds as is the case with many other agrienvironmental schemes.

Unfortunately, input taxes also entail some problematic issues. From an economics theory perspective, it is troubling that input taxes are not cost-effective. The reason for this is that the incentive is on economizing with the input use while cost effectiveness is based on equimarginal costs measured relative to emissions.

Additional benefits and disadvantages are specific to the input being taxed. In a eutrophication context, nitrogen fertilizer taxes are particularly relevant. A major disadvantage is that farmers and fertilizer producers are strongly against such taxes, which frequently delays their implementation or leads to insufficient tax levels. Second, they are perceived as unfair—farmers with excess nitrogen owing to intensive livestock production escape the tax, even though many studies suggest that intensive livestock production is the major cause of eutrophication from agriculture (McSweeny and Shortle 1989, Oenema 2004). There are numerous studies on nitrogen fertilizer taxes. An early study is Hanley (1990) while Vatn et al. (2006) is a fairly recent study. Common features for most of the studies on nitrogen fertilizers are that they succeed in reducing nitrate leaching and that the social costs are low, although not cost-effective according to the definition of cost effectiveness.

A particular concern related to high input taxes relates to the emergence of illegal markets or smuggling. Although this may not be a major issue for fertilizer taxes, it is for pesticides: modern pesticides are often highly concentrated and a liter of pesticide may be sufficient for several hundred hectares. Pesticides are therefore a high-value low-volume commodity, which makes it easy to smuggle from areas where they are not taxed heavily. This may cause a mismatch between official figures for use and measurements of pesticide residues, which in turn may cause difficulties establishing a reliable knowledge base for their environmental impacts.

4.5.5 Regulations Seeking to Solve the Asymmetric Information Issues[1]

As mentioned in Sect. 4.3, it is costly and technically difficult to measure nonpoint source emissions from individual farm fields. This is a major reason for the widespread use of procedural regulations in agriculture, and economists' interest in input taxes in agriculture, in particular on nitrogen fertilizers. The theoretical shortcomings of procedural and input regulations have led economists to search for ways to assess emissions and hence tax emissions. There are three main approaches in the economics literature on this issue that are briefly discussed in the following subsections.

4.5.6 Ambient Taxes

Segerson (1988) proposes to measure water quality in a recipient and issue an ambient tax on all farmers emitting to this recipient. In an *ambient tax*, the tax rate for all agents is decided based upon the marginal value of the last unit of emissions. Although this yields a cost-effective solution, it also means that excess tax revenues are collected. This has given birth to an own strand of the literature, where one seeks to reduce the excess taxation while maintaining cost effectiveness. Hansen and Romstad's (2007) is one of the most recent papers on this topic. They propose an informational feasible self-reporting mechanism that is robust to cooperation among polluters while giving participating firms correct abatement incentives as well as giving entry--exit incentives that are correct to a first-order approximation. Suter et al. (2009) have tested ambient taxes experimentally. Contrary to the theoretical papers in this area, they find that firm size matters, suggesting that more work is needed on the theory side.

4.5.7 Teams Approaches

The basic idea in Romstad (2003) is that it is possible to measure an increase in nutrient concentrations on a segment of a river or a stream. By offering a contract to all farmers (the team) behind these emissions, it will in principle be possible to implement emission-based regulations, which would then result in a cost-effective solution. Farmers are likely to accept such a contract if they are better off with the contract than with the standard nonpoint source regulations. Conditions for the team to function are established. An important driver in the mechanism is that dissatisfied members of the team can get out of the contract in the next time period. This exit possibility disciplines team members so that each member meets his or her part of the internal agreement among team members. A variant of the mechanism has been tested experimentally (Taylor et al. 2004).

4.5.8 Emission Taxes Based on Bodeled Emissions

Romstad (2012) suggests base regulations on model estimates of the environmental impacts. This is possible as environmental assessment models have gradually become reliable and

[1] Xepapadeas (2011) provides an updated theoretical review of the information issues of nonpoint source emissions, and ways to cope with these issues.

produce more accurate impact estimates. For biological systems, such models may also be used to decompose overall environmental impacts into natural and man-made effects. The basic idea of the paper is to offer farmer contracts to reduce nonpoint source with various price tags attached. Rather than requiring certain practices, a farmer who accepts the contract is willing to let his/her runoffs be calculated by a model based on the measures the farmer reports as implemented, which then leads to farmer paying based on the calculated runoffs from the model. Two types of contracts are envisioned: (1) where the farmer is held responsible for year-specific calculated runoffs (the most demanding contract type that triggers a higher upfront payment) and (2) where the farmer is held responsible for average calculated runoffs (the least demanding contract type with a lower upfront payment). Models under the Eutropia research project (http://www.mn.uio.no/kjemi/english/research/projects/eutropia/index.html) will be used to test the feasibility of the proposed mechanism.

4.5.9 Computable Nonpoint Source Integrated Modeling

In the last 20–30 years, several nonpoint emission projects have been initiated where economic modeling has been integrated with natural science models. This brief overview covers some of those models that have appeared repeatedly in the literature. There are two main types of models, farm-level (micro) models and sector models. Both modeling approaches have the advantages and disadvantages.

The strong side of farm-level (micro) models is their close interaction with the natural science models (nutrient turnover, erosion, hydrology, and plant growth), which makes these models well suited as a meeting platform between natural scientists and economists. Their main weak side is that they do not explicitly model sector-wide changes. The main reason for this is that farms do not change type, i.e., a dairy farm remains a dairy farm throughout the modeling exercise. EcEcMod (Vatn et al. 1997) and its follow-up, EcEcMod 2.0 (Vatn et al. 2006) are well-documented examples of this type of models. Economics modeling techniques involve a combination of nonlinear, mixed integer, and linear programming, where optimization takes place at the farm level, crop selection is endogenous (among allowable crops for that farm type), and manure storage and handling is consistent with tillage practices for model farms with livestock. The EcEcMod modeling system is no longer maintained.

The strong side of sector models is that they are able to endogenously capture changes in the agricultural sector. Their main weak side is that the integration with the natural sciences is weaker than for the farm models. Schou et al. (2000) is an example of such a model. Several sector models have been fitted to project sector figures of nutrient use to model farms. CAPRI (Leip et al. 2011) is one example of this approach.

The EU project Seamless combined the rich model interface of farm-level (micro) models and the endogenous treatment of farm types in sector models. Although the up- and downscaling issues of such a modeling exercise have been solved (Pérez Domínguez et al. 2009), the availability of detailed farm models at the European level was too limited to really test the procedure. This work continues through the Seamless Association (http://www.seamlessassociation.org/).

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Eutrophication of Lakes

5

Marcos Callisto, Joseline Molozzi and José Lucena Etham Barbosa

Abstract

Human activities and the unplanned occupation of land in aquatic basins can drive cultural eutrophication, which leads to the degradation of water quality, an increase in the concentrations of nutrients, and the depletion of biodiversity. This chapter will describe the basic concepts of trophic status, ecological changes, and alterations to the composition of freshwater biodiversity, as well as current threats and global perspectives of these issues. Additionally, selected case studies from Brazilian freshwater using benthic macroinvertebrates in urban reservoirs and cyanobacteria in semiarid lentic ecosystems are discussed.

Keywords

Eutrophication · Human alteration · Biodiversity loss

5.1 Introduction

Throughout the last few centuries, human use of freshwater resources for a variety of purposes has resulted in the degradation of aquatic ecosystems (Tundisi and Matsumura-Tundisi 2003). Increasing human populations and the expansion of industrial and agricultural activities have been important driving factors for the rapid deterioration of freshwater ecosystems. These impacts have resulted in water bodies with poor water quality and limited potential uses (Straskraba and Tundisi 1999).

The unplanned human occupation of aquatic basins can deteriorate water quality and limit the quantity and availability of freshwater resources, although the scale of this impact can vary with the economic and social organization of a particular region (Tundisi et al. 1991). Human activities tcan also often result in a considerable increase in nutrient concentrations in aquatic ecosystems, especially nitrogen and phosphorus, which can lead to the process of cultural eutrophication (Callisto et al. 2004).

Cultural eutrophication, which follows a clear sequence of cause and effect, can disrupt the homeostasis of lake ecosystems and result in an imbalance between the production, consumption, and decomposition of organic matter (Esteves 2011). Thus, algae and macrophyte blooms are often observed in eutrophic systems and can be responsible for the diminished multiple uses of lentic ecosystems. Additionally, a bloom of primary production is one of the main difficulties in the treatment of water for human consumption or industrial utilization (Tundisi et al. 1993). These ecological changes, including altered physical and chemical characteristics, can lead to changes in biological communities and a drastic loss of freshwater biodiversity (Barbosa et al. 1998; Maberly et al. 2002; Callisto et al. 2004, 2005).

Water quality biomonitoring programs commonly use benthic macroinvertebrates as bioindicators of environmental pollution, in addition to utilizing a suite of chemical, microbiological, and toxicological tests of water quality (Valdovinos and Figueroa 2000; Callisto et al. 2001). Benthic

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macroinvertebrate communities have frequently been used in assessments of human impacts on freshwater (Rosenberg 1992; Junqueira et al. 2000; Brooks et al. 2001; Fleituch et al. 2002). The use of bioindicators to assess water quality is based on the response of the organisms to changes in their environment, including perturbations of human or natural origins, and reflects their lifestyle and sedimentary behavior (Bonada et al. 2006).

There are many benefits of using benthic macroinvertebrates for biomonitoring programs: (a) they are easily collected and identified at the family or genera levels; (b) many taxa are sedentary and possess long life cycles, making them capable of registering cumulative effects on their habitats, and (c) they are sensitive to physical and chemical changes in ecosystems, and their responses to these alterations are detectable and measurable (Barbour et al. 1996).

There are a variety of benthic organisms that are frequently highly abundant in reservoirs; these organisms include Chironomidae, Oligochaeta, Bivalvia, Hirudinea, and Chaoboridae (Takeda et al. 1990; Brooks et al. 2001; Martins-Montanholi and Takeda 2001; Santos et al. 2006). Chironomidae larvae exhibit a high diversity of ecological features and are capable of surviving in many different environmental conditions, where some species are tolerant or sensitive to low oxygen concentrations, extremes of temperature, pH, salinity, and trophy (Prat et al. 1992; Henry 1993; Cranston 1995).

5.2 Basic Concepts

5.2.1 Lake Aging

Lake aging is a natural process that occurs on a geologic timescale and results in the lake being filled with materials that are eroded and transported by tributaries, deposited from the atmosphere and produced in the lake. Differences in runoff and watershed characteristics cause lakes to fill-in at different rates. The didactic natural succession is from lake to pond, pond to marsh, marsh to meadow, and meadow to dry land.

5.2.2 Brazilian Lacustrine Ecosystems

In Brazil, most lacustrine ecosystems are characterized as lagoons owing to their geomorphological origin related to the meanders of large rivers, coastal lagoons near the sea in the "restinga" formation, or in the floodplains of Amazonia and the Pantanal. Some deep lakes can be found in the Minas Gerais State in southeastern Brazil that originated in the curves of the Doce River (Barbosa et al. 1999).

5.2.3 Anthropogenic (Cultural) Eutrophication

Human land use, deforestation, and untreated sewage disposal are common causes of eutrophication in freshwater. Originally, eutrophication was known as the increased productivity of a lake as it ages. Often, an increased nutrient supply from human activities results in an increase in the biological production of the lake. Although the increased production may increase the rate of lake filling, it is incorrect to define eutrophication as lake aging. A lake does not die when it reaches a state of high productivity, but rather when it has been completely filled in and no longer exists. Lake filling results from production that occurs within the lake, which may increase with eutrophication, and from the deposition of organic and inorganic materials from outside the lake, which is not related to lake eutrophication.

5.3 Too Much of a Good Thing

Natural eutrophication is a fairly slow and gradual process that typically occurs over a period of many centuries as natural disturbances cause an imbalance between production and consumption within the lake, and the lake slowly becomes overfertilized. Although natural eutrophication is not rare in nature, it does not occur frequently or quickly. However, cultural eutrophication has become so common that the word "eutrophication" has come to mean a very harmful increase and acceleration of nutrient concentrations within a water body. The situation is as if something receives too much fertilizer or has too much of a good thing.

5.3.1 What is Meant by Trophic State?

In temperate regions, the term "trophic" originally referred to the nutrient status of an ecosystem. Esteves (1988) discussed the misuse of the lake typology approach in tropical regions and argued that it is necessary to consider the naturally high nutrient concentrations in tropical lakes. His paper, titled "Considerations on the application of typology of temperate lakes to tropical lakes," stressed the inadequacy of its application. The metabolic patterns of tropical lakes are completely different than temperate lacustrine ecosystems. When the basic indicators used in the typology of temperate lakes are applied to tropical lakes, the resulting classification may cause the same ecosystem to be placed into different categories.

Thienemann (1913) was the first author to use the distribution of benthic chironomid larva to classify lakes in Germany and, later, to propose his typology. In his studies of volcanic lakes in the Eifel region, he discovered a different

distribution of *Tanytarsus* and *Chironomus* genera in lakes. The *Tanytarsus* genus was found to occur at a higher density in lakes with oxygen that was well distributed throughout the water column during the summer period of thermal stratification. On the other hand, the *Chironomus* genus was abundant in deeper waters with lower oxygen levels during the same stratified period. Thienemann called the former category of lakes "alpine lakes" because of their similarity to lakes in the Alps, and the latter category "Baltic lakes" because they were similar to lakes in the Baltic zone in northern Germany. As Esteves (1988) described, the Eifel lakes may be considered to be the origin of all modern typology.

Almost one decade later, Naumann (1921) used phytoplankton and concentrations of phosphorus, nitrogen, and organic matter in the water and sediments to classify Swedish lakes. This researcher used the same classification scheme that was used for soils during that period and proposed the term "oligotrophic" to describe lakes with low nutrient concentrations of P, N, and organic matter and low densities of algal populations. Additionally, Naumann applied the term "eutrophic," which was typically used to describe fertile soils, to lakes with high concentrations of these characteristics. Further studies by Thienemann (1928) and Naumann (1930) classified the alpine lakes as oligotrophic and the Baltic lakes as eutrophic.

Most tropical lakes are shallow and show circulation patterns that are different from those in temperate lakes. These patterns, coupled with the higher temperatures, result in a unique metabolism in tropical lakes. In general, lakes are divided into three trophic categories: oligotrophic, mesotrophic, and eutrophic. The prototypic oligotrophic lake is a large deep lake with crystal clear water and a rocky or sandy shoreline. Both planktonic and rooted plant growth are sparse and the lake can support a coldwater fishery. A eutrophic lake is typically shallow with a soft and mucky bottom. Rooted plant growth is abundant along the shore and into the lake and algal blooms are not unusual. Water clarity is generally poor and the water often has a tea color. If the lake is deep enough to thermally stratify, the bottom waters are often devoid of oxygen. A mesotrophic lake has an intermediate trophic state with characteristics between the other two.

5.4 Current Threats

Although the response of any given water body to environmental changes will be unique, as some lakes are relatively resistant to change and others are more sensitive, one or more of the following factors can potentially reduce biodiversity in a eutrophic ecosystem (http://www.strategy.sebiodiversity.org.uk/pages/eutrophic-lakes.html):

- *Climate change:* A substantial change to the supply of water to an aquatic ecosystem would alter the characteristics of that water body, whereas an increase in temperature would produce wide-ranging effects, including accelerated plant growth.
- *Pollution:* Pollutants such as organic and inorganic fertilizers and nitrogen-rich gases can enter a water body from both point sources and diffuse sources. Increasing concentrations of these pollutants can cause nutrient enrichment (eutrophication) that can damage plant and animal communities. In general, pollution inputs from diffuse sources are greater than inputs from point sources.
- *Changes in land cover:* These changes can potentially result in the release of nutrients from soil that can then cause enrichment of water bodies. In addition to causing an increase in pollution, the long-term effects of such land use changes can also include siltation, which can smother fish spawning sites and damage aquatic vegetation. These problems are exacerbated by the removal of vegetation and reed swamps at the edges of a water body, which can act as nutrient sinks and effective barriers against particulate matter.
- *Water extraction:* Water may be extracted, either directly from a standing water body or from surface feeders or aquifers, for use as a potable supply or in industry or irrigation applications. Removing water from the system can decrease water levels and result in increased retention times and reduced flushing rates. This may exacerbate nutrient enrichment, cause deterioration of marginal vegetation through drawdown and cause shallow lakes to dry out. For coastal sites, a reduction in the throughput of fresh water could increase the salinity of a water body.
- *Fishing:* The introduction of fish, the removal of predators, and the manipulation of existing fish stocks for recreational fishing can lead to the loss of natural fish populations and may affect plant and invertebrate communities. Heavy stocking of bottom-feeding fish such as carp (*Cyprinus carpio*) can increase turbidity levels and accelerate the release of nutrients from sediments. This effect has been shown to cause major enrichment problems in some eutrophic water bodies.
- *Recreation:* The use of standing water for recreational and sporting purposes may disturb existing bird populations. Marginal vegetation may be negatively impacted by trampling and the action of boat hulls and propellers can destroy aquatic plants and stir up sediments, which can contribute to enrichment and algal growth. Additionally, the construction of marinas and other leisure facilities may destroy valuable habitat and can lead to increased pollution.
- *Nonnative plants and animals:* The release of nonnative plants and animals can be very damaging to aquatic ecosystems. As an example, the introduced signal crayfish (*Pacifastacus leniusculus*) has destabilized the biota of some water bodies by consuming large amounts of

aquatic vegetation and it has eliminated many populations of native crayfish by spreading crayfish plague.

5.5 International Perspective

Cultural eutrophication, which is the excessive growth of plants caused by anthropogenic nutrient enrichment, is recognized as the primary problem facing most surface waters worldwide (Smith and Schindler 2009). The main driving factors of cultural eutrophication are anthropogenic changes to land use in the catchments and nutrient inputs from untreated sewages (Tundisi and Matsumura-Tundisi 2003). For example, clearing forested catchments causes the long-term loss of nutrients from the landscape, and these nutrients can end up in the local water bodies. Applications of manure or commercial fertilizer further increase terrestrial nutrient exports. Fertilized soils can become nutrient saturated and these nutrients can leak into receiving waters for decades after the external nutrient additions are reduced or discontinued. The main potential effects of cultural eutrophication caused by excessive inputs of phosphorus and nitrogen into fresh and coastal waters are as follows:

- Increased biomass of phytoplankton and macrophyte vegetation.
- Increased biomass of consumer species.
- Shifts to bloom-forming algal species that might be toxic or inedible.
- Increased biomass of benthic and epiphytic algae.
- Changes in species composition of macrophyte vegetation.
- Increased incidence of fish kills.
- Reductions in species diversity.
- Reductions in harvestable fish and shellfish biomass.
- Decreases in water transparency.
- Taste, odor, and drinking water treatment problems.
- Oxygen depletion.
- Decreases in the perceived esthetic value of the water body.

5.6 Eutrophication and Infectious Disease Risk

There is a direct link between eutrophication and disease risk. Water-related diseases are a major cause of human morbidity and mortality worldwide, and recent evidence suggests that diseases can have a major impact among aquatic organisms. Clearly, biological waste disposal activities, such as manure applications to cropland, can simultaneously increase the loading of phosphorus, nitrogen, and potentially hazardous coliform bacteria to surface waters. However, enhanced nutrient loading may be sufficient on its own to influence the abundance, composition, virulence, and survival of pathogens that are already present in aquatic ecosystems. Another potential nutrient--pathogen interaction involves changes in food quality. For example, if eutrophication influences the nutrient content of food consumed by host organisms, then changes in host nutrition could alter host–pathogen dynamics and ultimately result in infection. These potential links between pathogens and nutrient availability could also be important for managing human health in streams and rivers with significant bathing-related activity. Recreational use of waters can spread fecal-oral viruses (e.g., enteroviruses, hepatitis A viruses, rotaviruses and others) that cause a broad range of gastrointestinal, respiratory, eye, nose, ear, and skin infections.

5.7 Eutrophication of Brazilian Freshwaters

5.7.1 A Case Study of Reservoirs

The Ibirité reservoir (19°07′00″–20°02′30″S, 44°07′30″–44°05′00″W) was built in 1968 at an altitude of 773 m a.s.l. This reservoir has an area of 2.8 km^2, a water volume of 15,423,000 m^3, and an average depth of 16 m. Most of the hydrographic basin of the Ibirité Reservoir spans the municipalities of Ibirité (148,535 inhabitants) and Sarzedo (23,282 inhabitants). The landscape of the reservoir basin is dominated by Eucalyptus plantations, a large condominium complex, small farms, and several industrial plants (Pinto-Coelho et al. 2010; Fig. 5.1).

The Vargem das Flores reservoir (19°53′30″–19°55′25″S, 44°07′22″–44°10′59″W) was built in 1971 and is situated at 838 m a.s.l. The reservoir has a water surface of 5.5 km^2, a water volume of 44,000,000 m^3, and a maximum depth of 18 m. The maximum level sill spillway is 838.64 m with a hydraulic retention time of 365 days. Approximately 12.3 ha of the Vargem das Flores reservoir basin was designated as an environmentally protected area (EPA) by law 16.197/06 (Minas Gerais, Brazil; Fig. 5.1).

The Serra Azul reservoir (19°54′09″–20°00′52″S, 44°23′16″–44°30′20″W), which has been operating for approximately 30 years, is located at an altitude of 760 m a.s.l., has a water surface of 8.9 km^2, a water volume of 93,000,000 m^3, and a maximum depth of 40 m. The maximum level sill spillway is 760 m with a hydraulic retention time of 351 days. This reservoir, together with the Vargem das Flores reservoir, provides the primary drinking water supply to the metropolitan region of the State's capital (ca. 4.8 million people). The protection area of the Basin is 27,200 ha, and the territory's domain Companhia de Saneamento de Minas Gerais (COPASA) is 3,200 ha (COPASA 2000; Fig. 5.1).

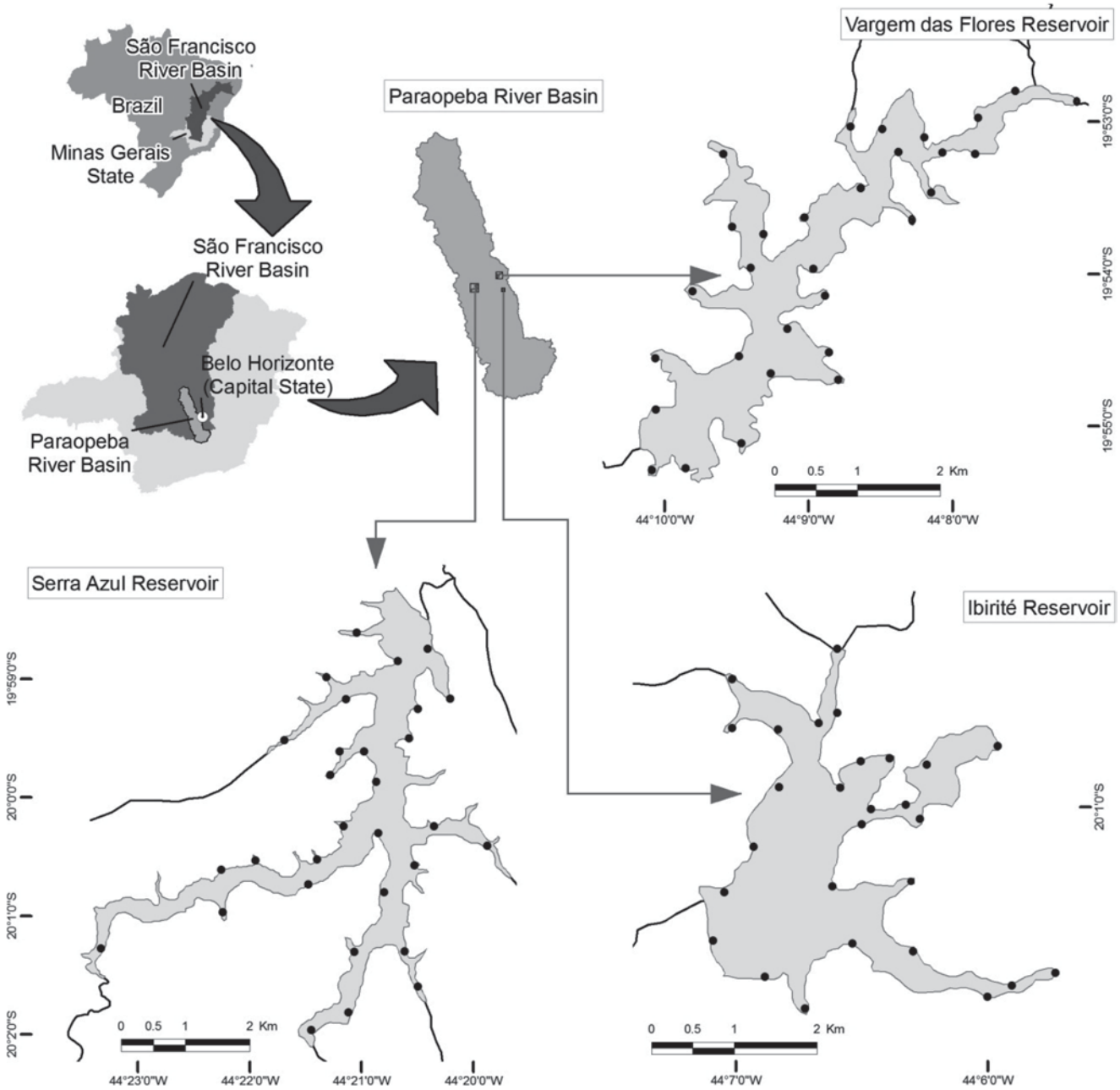

Fig 5.1 Location of the Vargem das Flores, Serra Azul, and Ibirité reservoirs in the catchment of the Paraopeba River, Minas Gerais, Brazil and the distribution of the sampling sites (*black dots*) within the reservoirs

5.7.2 Macroinvertebrate Sampling

Macroinvertebrate samples were collected from 90 sites in the littoral zone of the three reservoirs. Samples were collected quarterly over a period of 2 years (in March, June, September, and December of 2008 and 2009) with an Ekman-Birge dredge (0.0225 m^2). The material collected was fixed in 70% formaldehyde and subsequently identified to the family or genus level, as was the case of Chironomidae (Peterson 1960; Merritt and Cummins 1996; Mugnai et al. 2010; Trivinho-Strixino 2011).

5.7.3 Abiotic Data

The following physical and chemical parameters of the surface water were measured using a YIS model Multiprobe for each sampling occasion at each sampling site: electrical conductivity, turbidity, total nitrogen (TN), and pH. Additionally, groundwater samples were collected with a Van Dorn-type cylinder for subsequent measurement of total phosphorus (TP) and orthophosphates (PO_4) for use in the trophic state index (TSI), following the "Standard Methods for the Examination of Water and Wastewater" (APHA 1992). The

concentration of chlorophyll *a* (Chla) was obtained according to Golterman et al. (1978) and the transparency was estimated using a Secchi disc (S). Additionally, large seasonal variations of temperature and rainfall were evaluated during the sample period. The average monthly values of temperature and precipitation were calculated for all the sampling periods based on data from the Brazilian National Institute of Meteorology (INMET) for the metropolitan region of Belo Horizonte in 2008 and 2009.

The Carlson (1977) TSI, modified by Toledo et al. (1983), was calculated for each of the sites. Each index is composed of subindices, which are then weighted to obtain a final value of the trophic status. The TSI is calculated with the following formula:

$$\mathrm{TSI} = \mathrm{TSI(S)} + 2 \times \left[\frac{\mathrm{TSI(TP)} + \mathrm{TSI(PO_4)} + \mathrm{TSI(Chla)}}{7}\right]$$

where the subindices are defined as follows:

$$\mathrm{TSI(S)} = 10 \times \left(6 - - \left(\frac{0.64 + \ln \mathrm{S}}{\ln 2}\right)\right),$$

$$\mathrm{TSI(TP)} = 10 \times \left(6 - \left(\frac{\ln\left(\frac{80.32}{\mathrm{TP}}\right)}{\ln 2}\right)\right),$$

$$\mathrm{TSI(PO_4)} = 10 \times \left(6 - - \left(\frac{\ln\left(\frac{21.67}{\mathrm{PO_4}}\right)}{\ln 2}\right)\right),$$

$$\mathrm{TSI(Chla)} = 10 \times \left(6 - - \frac{2.04 - -0.695 \ln \mathrm{Chla}}{\ln 2}\right).$$

Based on this calculation, TSI values ranging from 0 to 44 correspond to oligotrophic waters; values from 44 to 54 are mesotrophic waters, and a value of greater than 54 are eutrophic waters.

5.7.4 Macroinvertebrate Sampling

In total, 14,425 organisms, belonging to 47 taxa (4 Mollusca, 2 Annelida, and 41 Arthropoda), were collected from the 90 sampling sites during the 2-year observation period. Of the total number of organisms sampled, 24% were Diptera larvae, where *Chironomus* (8%), *Tanypus* (4%), and *Coelotanypus* (4%) were the most representative genera.

The lowest numbers of organisms were found in the oligotrophic Serra Azul reservoir (2,438 organisms), followed by the Vargem das Flores reservoir (mesotrophic, 5,033 organisms) and Ibirité reservoir (eutrophic, 6,954 organisms). Following the construction of a reservoir, great changes can be expected in the physical and chemical characteristics of the water and in the functional and structural composition of aquatic communities, including a reduction of the total number of species and the establishment of exotic species (Yanling et al. 2009).

The colonization of highly modified new habitats, as in the case of reservoirs, is typically undertaken by highly resistant species that are adapted to stagnant waters, as well as generalist species that are small in size, have long life cycles, and have high rates of sexual maturation (Rueda et al. 2006; Ruse 2010). In our reservoirs, even in the selected sites with oligotrophic conditions, the observed taxa richness (51 taxa, 59% Diptera) was lower than on the river in the same drainage basin where 63 taxa were recorded, with Ephemeroptera, Plecoptera, and Trichoptera (EPT) representing 16% of the total individuals (A. Lessa, unpublished data). In our study, the presence of the exotic species *Melanoides tuberculatus* (Müller 1774; Thiaridae, Gastropoda) was recorded at sites with oligotrophic characteristics. Since it was first recorded in Brazil in 1967, this African-Asian species has extensively invaded tropical freshwater ecosystems and settled in various types of substrates (Dudgeon 1989; Clementes et al. 2006). The densities of *M. tuberculatus* in disturbed habitats are likely to increase and may surpass the level of 10,000 ind m^{-2} (Santos and Eskinazi-Sant'Anna 2010). Additionally, differences were found in the taxa composition of oligotrophic, eutrophic, and mesotrophic sites. Oligochaeta, including the above-mentioned *M. tuberculatus* and *Chironomus*, represented 60% of the total individuals in the more disturbed sites, while they only accounted for 7% of the total individuals in the oligotrophic sites (Fig. 5.2). In the Ibirité eutrophic reservoir, chironomids represented 29% of the samples.

Some genera of Chironomidae were found only in oligotrophic sites (*Manoa, Pseudochironomus*, *Stenochironomus*, *Zavreliella*, *Lauterboniella*, *Paralauterboniella*), which is a good indication that these sites may serve as reference sites for an ecological quality assessment of reservoirs in tropical areas.

Several authors have shown that different chironomid species have different sensitivities to stress (Davies and Jackson 2006; Arimoro et al. 2007; Roque et al. 2010). For example, the genus *Fissimentum*, which was observed with a high number of individuals in oligotrophic sites, is considered an indicator of good water quality (Cranston and Nolte 1996). An evaluation of the spatial distribution of taxa showed that when both Oligochaeta and Chironomidae had the highest occurrence of organisms (ind m^{-2}) in a reservoir arm, this was potentially characteristic of an input of untreated sewage waste from the surrounding intense urban occupation (Fig. 5.3).

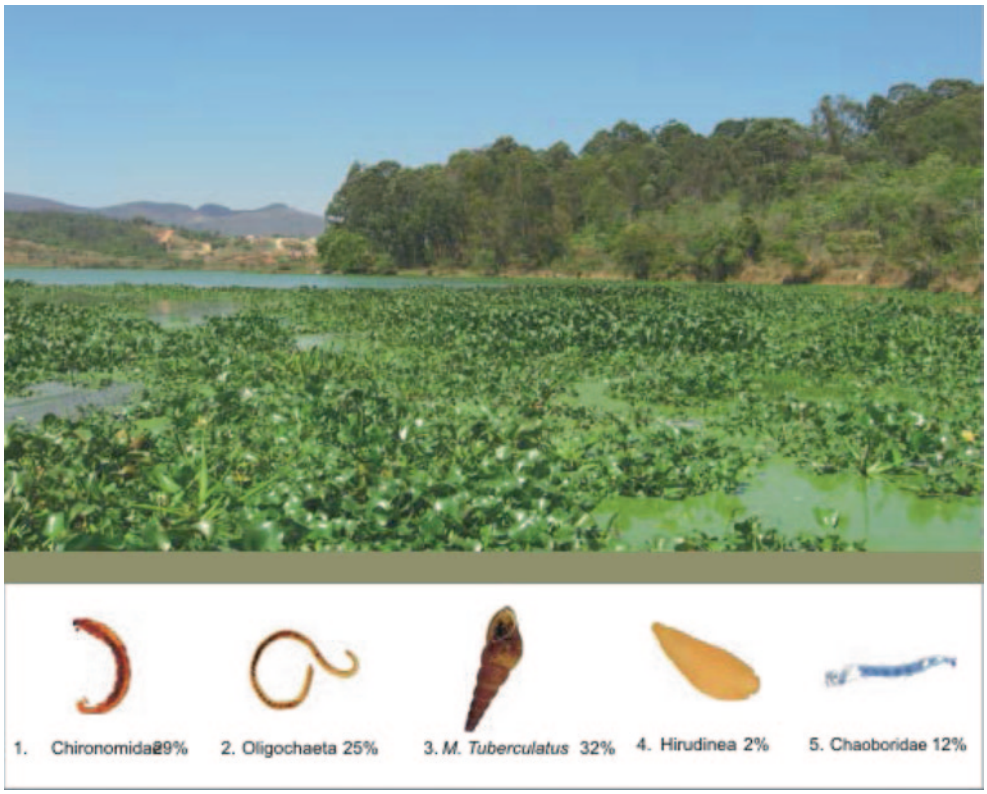

Fig. 5.2 Percentage of organisms found in the main Ibirité reservoir: *1*, *2*, and *4* are resistant taxa, *3* are alien species, and *5* are typical organisms of lentic environments

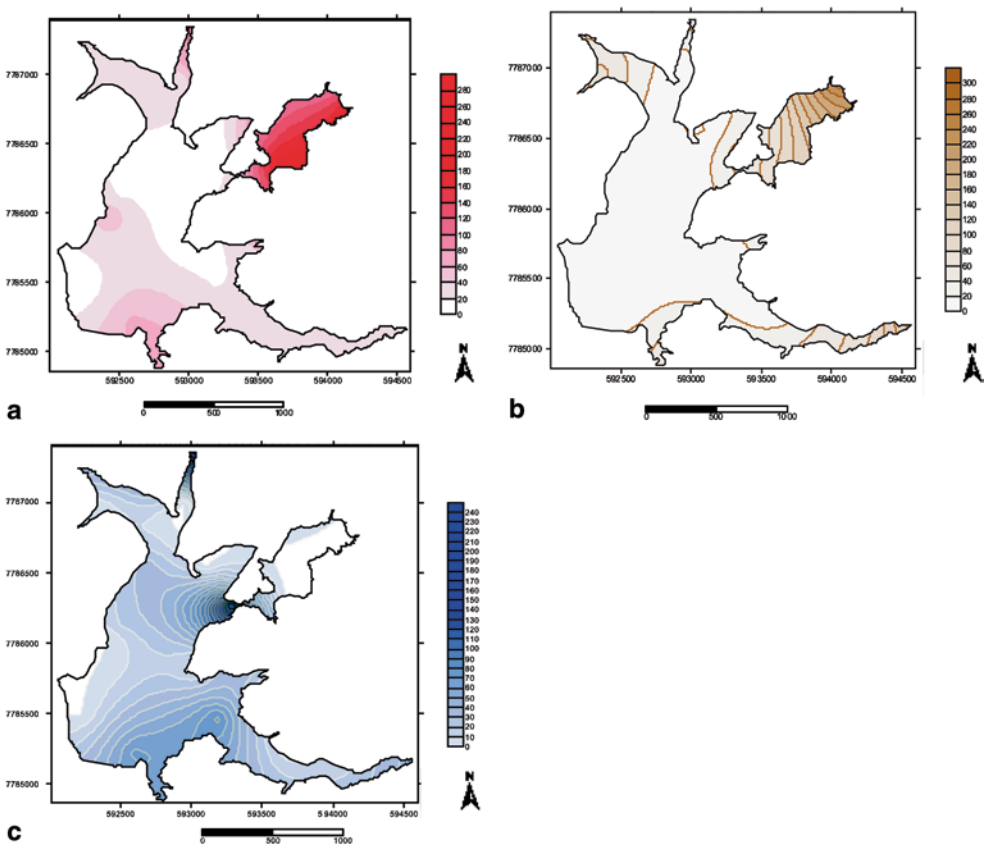

Fig. 5.3 Spatial distribution of organisms sampled in the main Ibirité reservoir: **a** Chironomidae, **b** Oligochaeta, and **c** *Melanoides tuberculatus*

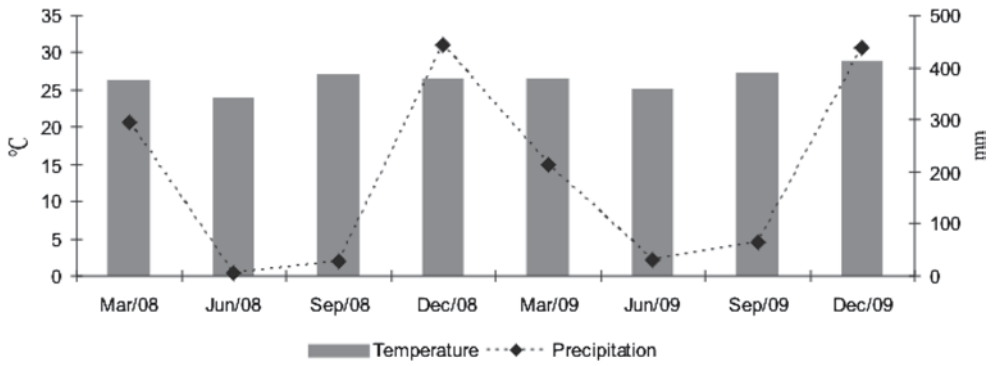

Fig. 5.4 Average monthly precipitation (mm, *bars*) and temperature (°C, *dots*) observed during the sampling periods

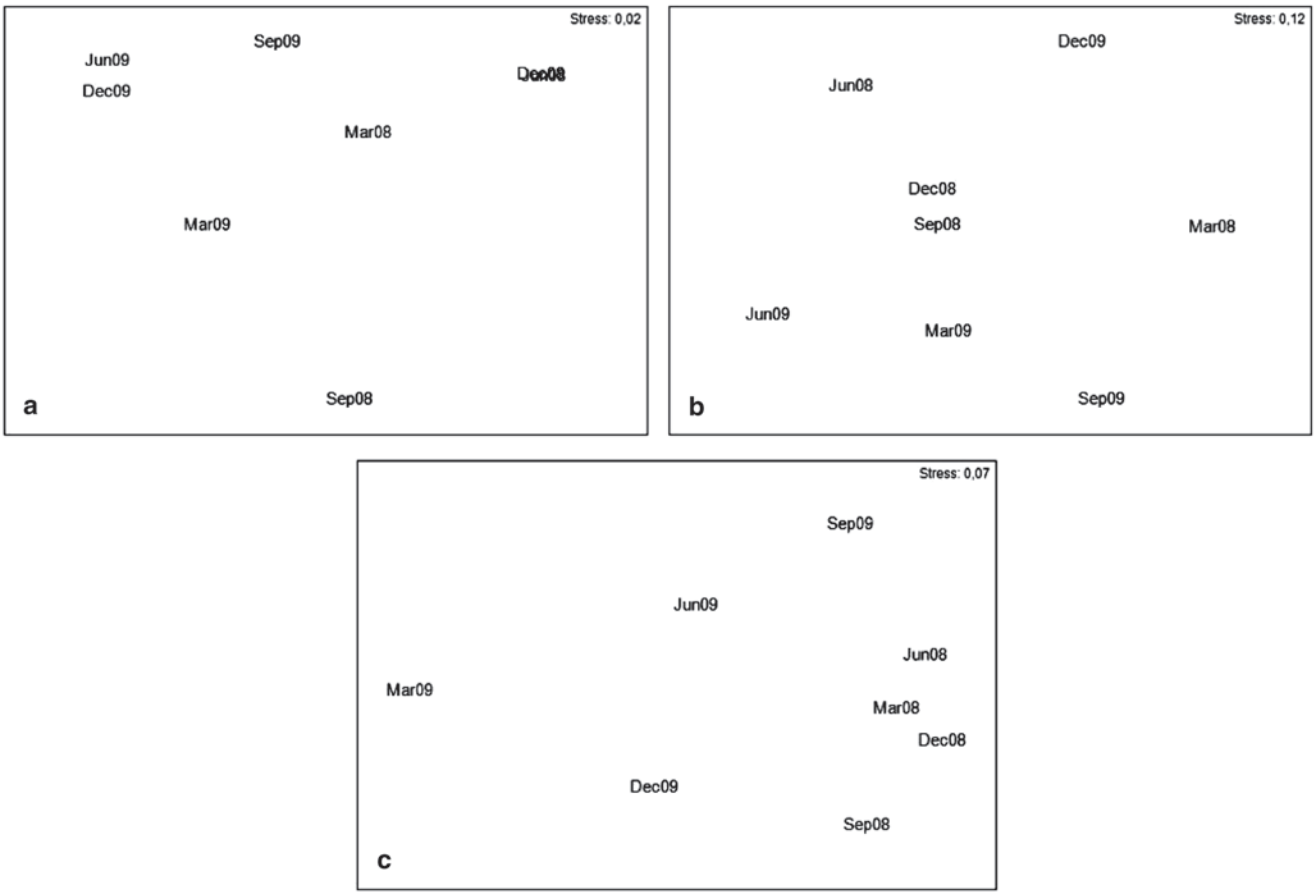

Fig. 5.5 Results of the 2nd-STAGE MDS for the three reservoirs based on biological data collected in December (Dec), March (Mar), June (Jun), and September (Sep) of 2008 (08) and 2009 (09) for the **a** Serra Azul, **b** Vargem das Flores, and **c** Ibirité reservoirs

5.7.5 Abiotic Data

The climatic data for 2008 and 2009 confirmed the existence of two distinct seasons: a wet season from December through March and a dry season from June through September. December 2008 had the highest rainfall average (442 mm), followed by January 2009 (282 mm). The driest months were June 2008 and June 2009, when no precipitation occurred. The maximum temperature during the study period was recorded in December 2009 (29.0 °C) and the minimum was recorded in June 2008 (23.9 °C; Fig. 5.4).

The 2nd-STAGE nMDS was consistent with the above findings, showing that there was no pattern of high correlation between the communities sampled in the same month of the year (e.g., December 2008 and December 2009) or the same season (dry and wet; Fig. 5.5). For rivers in both temperate and tropical regions, seasonal climate variability is accompanied by changes in the communities (Sporka

et al. 2006; Leunda et al. 2009; Puntí et al. 2009). Several previous studies (e.g., Feio et al. 2006; Aroviita et al. 2010) have shown that these changes are known to affect ecological assessments based on reference conditions that represent the systems only for a given season. However, the seasonal variability of temperature and precipitation observed during the 2 years of sampling in this study was not reflected in the benthic communities of the reservoirs. Seasonal variability in the communities was unpredictable and similar to the interannual variability. Other authors studying both subtropical systems (China) and temperate systems (Canada) have observed that rainfall and flood pulses did not influence the distribution of Chironomids in reservoirs because they are well adapted to fluctuations in the water level (Zhang et al. 2010; Furey et al. 2006).

The ANOSIM global R values for the three reservoirs showed wide variability within the sampling periods (ANOSIM Serra Azul: Global $R=0.054$, $p=0.001$; ANOSIM Ibirité: $R=0.166$, $p=0.001$; and ANOSIM Vargem das Flores: $R=0.113$, $p=0.001$). According to the TSI, 29 sites were classified as oligotrophic in the Serra Azul reservoir, and only one site was classified as mesotrophic. The Vargem das Flores reservoir had 26 sites classified as oligotrophic, with 1 site as mesotrophic and 3 sites as eutrophic. Over the 2 years of samples in the Ibirité reservoir, 28 sites were identified as eutrophic and 2 sites were mesotrophic (Fig. 5.6).

The environmental variables were found to have higher values in the eutrophic reservoir than in the oligotrophic reservoir. For example, the median electrical conductivity was 280.50 and 26.36 mS cm^{-1} for the eutrophic and oligotrophic reservoirs, respectively. The exception was for the S, which had the highest average values in the oligotrophic reservoir (see Table 5.1). The decrease in diversity of the benthic communities in the Ibirité reservoir can likely be explained by an increase in the trophic status owing to the land use and occupation of the areas surrounding this reservoir. The spatial distribution of some of the environmental variables showed that one arm of the reservoir had high concentrations of nutrients (TN and high levels of TN/TP; Fig. 5.7).

5.7.6 Semiarid Lentic Ecosystems

Hydrological fluctuations can cause significant changes to lakes and reservoirs in arid and semiarid regions, where both seasonal and annual variability can cause changes in the shape and size of the ecosystems (Sánches-Carrillo et al. 2007). The reservoirs in these regions can suffer significant intraannual variations of water volume, surface area, water residence time, and depth, which may affect their physical, chemical, and biological features.

In lakes located in temperate regions, phosphorus is the main limiting resource of primary productivity and the concentration of phosphorus in the water is correlated with algae biomass (Dillon and Rigler 1974; OECD 1982). On the other hand, Thornton and Rast (1989, 1993) showed that reservoirs from semiarid regions respond differently to eutrophication than do lakes in temperate regions, from which the classical concepts of eutrophication were developed. Thus, the primary functions that influence the limnological dynamics may not be similar between these two regions, and, therefore, system responses to nutrient enrichment may be different (Thornton 1990; Tundisi et al. 1990).

Because the TSI was developed in temperate lakes, its application to tropical reservoirs has been widely questioned (Bouvy et al. 2000; Huzsar et al. 2000; Costa et al. 2006; Panosso et al. 2007). Thornton and Rast (1993) proposed that concentrations of TP above 60 μg l^{-1} and Chlaabove 12 μg l^{-1} are indicative of a eutrophic reservoir in semiarid regions. This designation is set at the point where the algal biomass would be limited more by light than by the concentration of phosphorus.

A typical phenomenon in eutrophic lakes is the occurrence of blooms of cyanobacteria, which are common planktonic organisms living in different aquatic ecosystems. Although they are primarily related to eutrophication (Watson et al. 1997), their distribution is not limited to high-productivity ecosystems (Reynolds 1997). Cyanobacteria blooms are globally distributed and are regulated by many environmental variables linked by geographical and ecological aspects (Ferrão-Filho et al. 2009).

Cyanobacteria blooms affect water quality by changing the pH, transparency, and biodiversity, and by producing odors and/or toxins, such as cyanotoxins (Blahová et al. 2008). Toxic blooms of cyanobacteria are common in man-made lakes in the semiarid regions of Brazil and they frequently cause human health threats (Molica et al. 2005; Costa et al. 2006; Vasconcelos et al. 2011).

Although cyanobacteria blooms in reservoirs in semiarid Brazil are mainly related to the eutrophic conditions of these systems, other factors may also contribute to the success of cyanobacteria. These factors include environmental constancy, annual rain deficit and lack of water renewal, high temperatures, high pH, low N/P ratio, low ammonium concentrations, and the absence of efficient predators (Bouvy et al. 1999, 2000; Huszar et al. 2000, 2006; Barbosa et al. 2010; Dantas et al. 2010).

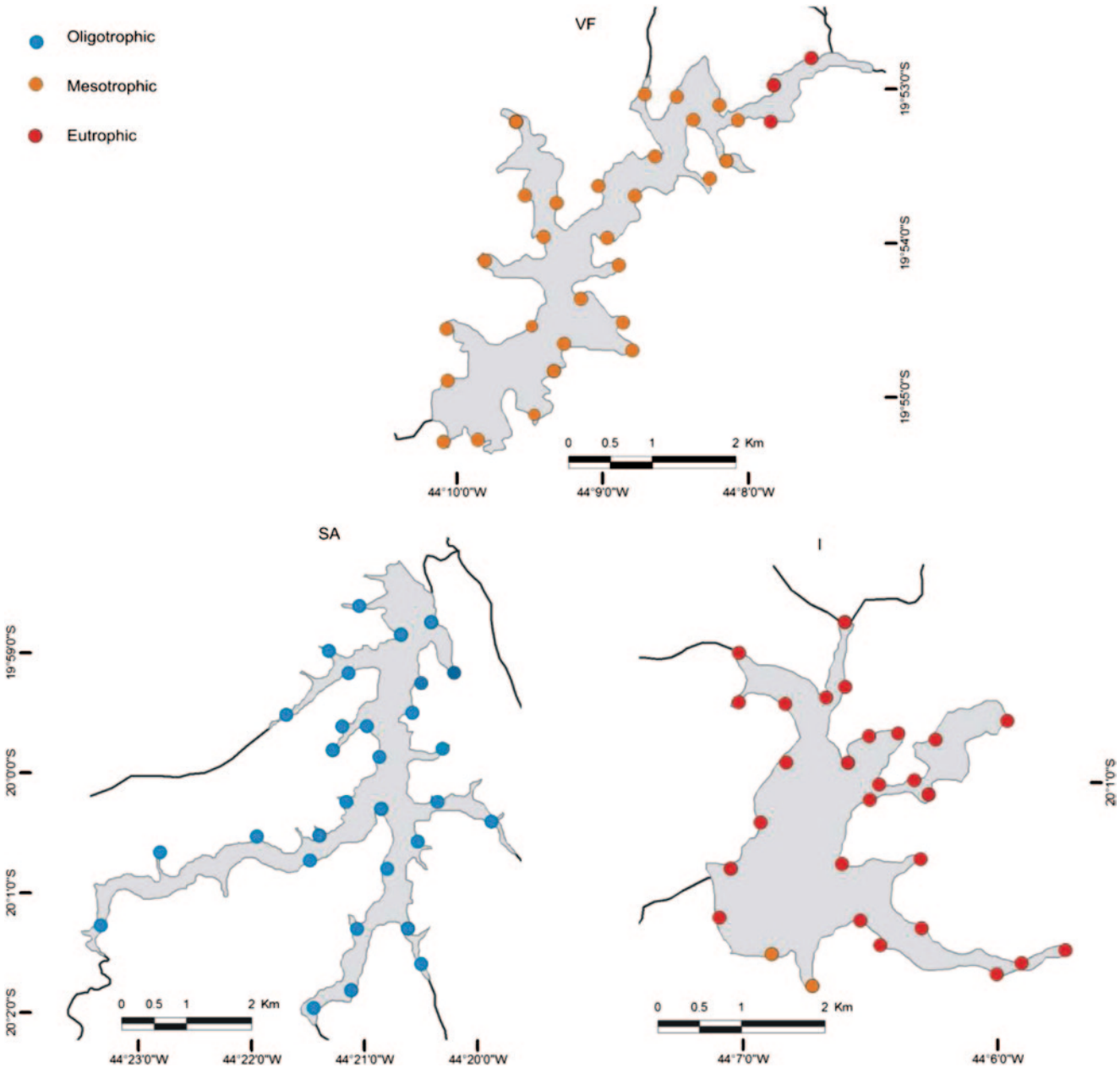

Fig. 5.6 Classification of sites according to the TSI index for the Vargem das Flores (VF), Ibirité (I), and Serra Azul (AS) reservoirs during 2008 and 2009

5.8 Case Study of the Trophic Evolution of a Reservoir Used to Supply the Citizens of the Paraíba State in the Semiarid Region of Brazil

5.8.1 Site Description

The water resources of the Paraíba State are distributed throughout 11 watersheds (Fig. 5.8), which contain more than 123 reservoirs. These reservoirs hold more than 15 million m^3 of water intended for use as the public supply and they provide a maximum storage capacity of nearly 43,906,773,462 m^3. The 20 reservoirs evaluated in this study are located between 6°48′ to 8°12′S and 38°33′ to 34°47′W (Fig. 5.8) and are present in two different hydrographic basins. The Paraíba and Piranhas River basins are the largest basins in the Paraíba State, and they represent the highest potential for water accumulation (28 and 67 %, respectively).

The climate classification of the reservoirs is BSwh, according to Koppen's classification system, which describes a semiarid hot climate with 7–9 dry months. The average temperatures are between 28 and 33 °C and the precipitation

Table 5.1 Environmental variables sampled in the oligotrophic, mesotrophic, and eutrophic reservoirs

Environmental variables	Oligotrophic	Mesotrophic	Eutrophic
Secchi disc (m)	2.34±0.86	1.4±0.7	0.47±0.27
Water temperature (°C)	27.98±3.65	25.9±2.57	27.5±3.65
pH	7.69±0.44	8.13±0.50	8.33±0.98
Electrical conductivity (mS cm^{-1})	26.34±8.66	135.94±27.36	280.50±114. 46
Total dissolved solids (mg l^{-1})	18.45±5.21	91.68±27.33	197.43±70.64
Turbidity (NTU)	5.05±10.29	15.48±28.06	55.78±66.71
Dissolved oxygen (mg l^{-1})	7.72±0.81	7.63±1.16	7.00±0.21
Chlorophyll a (μg l^{-1})	2.05±3.44	2.34±2.21	53.65±78.66
Total nitrogen (μg l^{-1})	0.05±0.04	0.22±0.25	0.29±0.21
Total phosphorus (mg l^{-1})	23.16±20.39	23.19±20.41	171.71±260.64
Orthophosphates (μg l^{-1})	7.21±5.12	7.90±5.82	22.62±86.78

The values represent the mean (±SD) of the 2-year sampling period

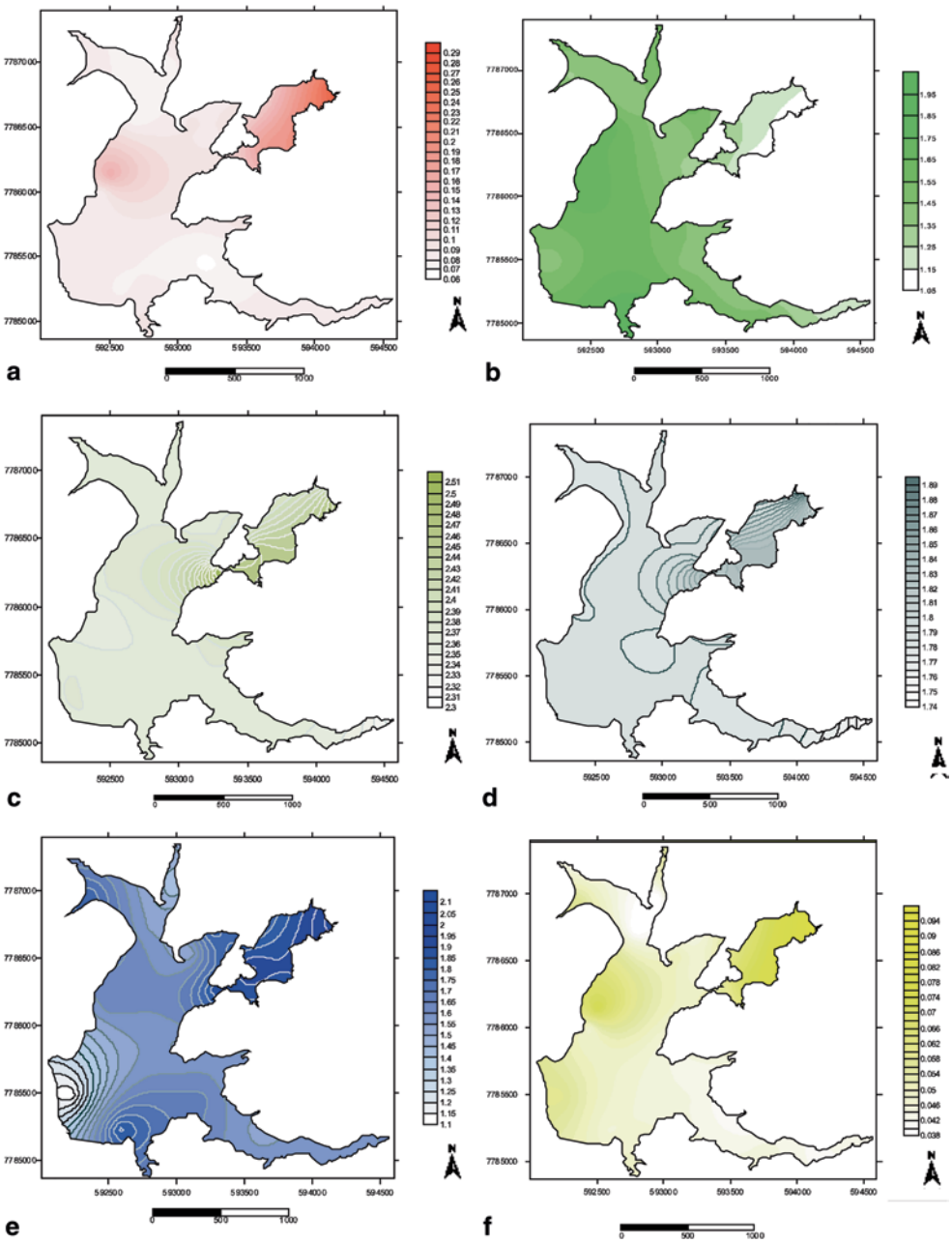

Fig. 5.7 Spatial distribution of some of the environmental variables in the Ibirité reservoir: **a** total nitrogen (μg l^{-1}); **b** chlorophyll a (μg l^{-1}); **c** electrical conductivity (mS cm^{-1}); **d** total dissolved solids (mg l^{-1}); **e** turbidity (NTU); and **f** ratio of total nitrogen to total phosphorus

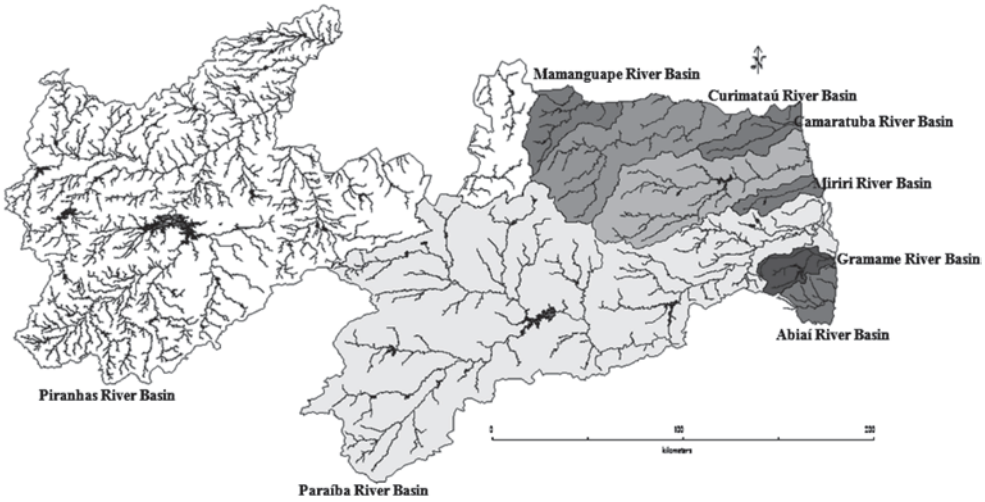

Fig. 5.8 Map of Paraíba State (Brazil), including the different hydrographic basins, and the locations of the sampled reservoirs

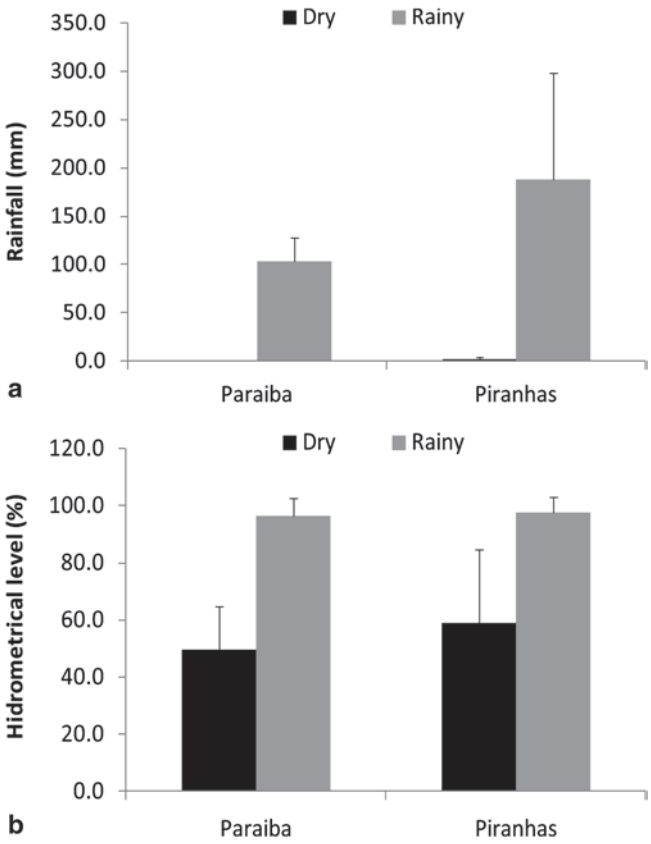

Fig. 5.9 Rainfall (**a**) and hydrometric levels (**b**) of the reservoirs during the dry and rainy seasons in the Paraíba and Piranhas River basins, Paraíba State, northeastern Brazil

is approximately 700 mm/year. In all the reservoirs, the dry periods occurred between August and March. These periods included low precipitation levels (40–280 mm), and the hydrometric levels of the reservoirs were generally low as well. During the rainy seasons, from May to July, the precipitation was higher (150–450 mm) and the reservoirs reached their maximum capacity. The wind velocity in the region was typically negligible and ranged from 3 to 4 m s^{-1}. The total annual evaporation varied between 2,500 and 3,000 mm with decreasing values trending from west to east.

Each of the 20 reservoirs was sampled eight times between August 2006 and August 2009, including sampling events in both the dry and rainy periods. During the dry periods, we observed low rainfall in the Piranhas (X = 2.1 mm) and Paraíba (X = 0.2 mm) River basins. The hydrometric levels of the reservoirs were generally low as well. In the Piranhas River, the hydrometric level of the reservoirs varied from 9.9 to 91.2 % of their total capacity, while in the Paraíba River, reservoirs ranged from 36.9 to 73.8 % (Fig. 5.9b). During the rainy seasons, the precipitation was higher in Piranhas River basin (X = 187.4 mm) than in the Paraíba River basin (X = 103.5 mm; Fig. 5.9a). During this period, 76 % of the reservoirs reached their maximum capacity in the Piranhas River basin, and only 40 % reached their capacity in the Paraíba River basin (Fig. 5.9).

5.8.2 Sample Collection

Environmental and phytoplankton samples were collected from one permanent site at the deepest part of each reservoir near the dam by holding a Van Dorn Bottle 10–20 cm beneath the water surface. Light transparency was assessed using an S. Temperature, pH, and electrical conductivity were measured using specific electrodes. Dissolved oxygen was measured by the Winkler method. Water samples were collected in PVC bottles that were previously cleaned with distilled water. The samples were transported to the laboratory on ice, where they were frozen and analyzed for nutrient concentrations (including inorganic dissolved nitrogen, dissolved reactive phosphorus, and TP) according to the procedures described by APHA (1992).

Table 5.2 Limnological measurements in the reservoirs

Piranhas River						Paraíba River				
Variables	Dry		Rainy			Dry		Rainy		
	Mean	CV (%)	Mean	CV (%)	*p*	Mean	CV (%)	Mean	CV (%)	*p*
Water temperature	29.9	6.72	29.57	8.93	0.74	28.2	6.49	28.2	3.96	0.93
Dissolved oxygen	7.95	13.4	7.008	11.5	0.01*	7.82	7.53	8.44	23.3	0.51
Alcalinity	20.4	24.4	17	28.7	0.09	29.2	24.5	18	18	0.01*
Inorganic dissolved nitrogen	7.49	212	75.07	121	0.01*	2.3	31.4	122	112	0.08
P-ortho	11.80	63.2	33.31	72.1	0.01*	70.2	71	92.6	64.8	0.53
Total-P	168.11	58.11	2.492	135	0.19	1,681.1	58.11	91.02	27.4	0.24

The mean and coefficient of variation (CV) are presented for the two sampling periods as well as the significance level of the differences between the dry and rainy season for Piranha and Paraíba Rivers (*p*)
*$p<0.05$

5.8.3 Data Analysis

Relationships between environmental parameters and the density of cyanobacteria were studied using multiple regression analysis. The Akaike's information criterion (Johnson and Omland 2004) was used to extract the variables that significantly increased the amount of explained variation ($\Delta AIC<2$).

An analysis of variance (ANOVA) indicated significant differences between the rainy and dry seasons for the reservoirs in the Piranhas River basin for dissolved oxygen, inorganic dissolved nitrogen, and TP. For the reservoirs in the Paraíba River basin, only alkalinity was found to have a significant seasonal difference (Table 5.2).

Differences of limnological factors were observed between the reservoirs in the Piranhas and Paraíba River basins, except for TP and total alkalinity (Table 5.2). In the dry season, the Piranhas River reservoirs showed higher mean values for temperature, dissolved oxygen, and dissolved inorganic nitrogen. Higher mean concentrations of TP were registered in the Paraíba River reservoirs. During the rainy season, the Paraíba River reservoirs had higher concentrations of dissolved inorganic nitrogen and TP (Table 5.2).

Reservoirs in semiarid regions are considered to be eutrophic when the annual average concentration of TP is higher than 60 μg l^{-1} (Thornton and Rast 1993). During the sampling period, an increase in the concentrations of TP in the reservoirs was observed, with averages ranging from 39.3 μg l^{-1} (DP = 12.76) in 2006 to 155.89 μg l^{-1} (DP = 81.16) in 2009. In 2006, 7.7% of the reservoirs were categorized as eutrophic and that percentage increased in each subsequent year, with 30.8% in 2007, 42.3% in 2008, and 57.7% in 2009 (Fig. 5.10).

We identified 188 taxa in the reservoirs, which were distributed among nine taxonomic groups: Chlorophyceae (61), Cyanobacteria (49), Bacillariophyceae (34), Euglenophyceae (14), Zygnemaphyceae (19), Dinophyceae (5), Chlamydophyceae (4), Xanthophyceae (1), and Oedogoniophyceae (1). No individual taxon was found to be present in all the sampled reservoirs. However, *Cyclotella meneghiniana*, *Cylindrospermopsis raciborskii*, *Aulacoseira granulate*, *Aphanocapsa elachista*, and *Pseudoanabaena limnetica* were the most frequently identified species. Out of the total number of identified taxa, 39 occurred only in the dry period and 30 were found only during the rainy period. *Aphanizomenon tropicalis* and *Coelastrum scabrum* were the most abundant of the 16 taxa that were found only in the Paraíba River, and *Dolichospermum spiroids*, *Merismopedia tenuissima*, and *Oocystis lacustris* were the most abundant of the 31 taxa found only in the Piranhas River.

The most abundant species of cyanobacteria in the reservoirs were potential toxin producers. These species dominated the phytoplankton community in 16 of the reservoirs, especially during the dry periods, and represented 73.1% of the total individuals and 54.08% of the total algae during the rainy season. The occurrence of cyanobacteria blooms in reservoirs increased significantly between 2006 and 2009. In 2006, only 3% of the reservoirs were found to have cyanobacteria blooms, while in 2007 that number grew to 20%, in 2008 it was 45%, and in 2009 it reached 62%. Most of the observed cyanobacteria blooms were found in the Piranhas reservoirs (Fig. 5.11).

A multiple regression analysis with cyanobacteria density as the dependent variable showed a positive relationship with dissolved oxygen and a negative relationship with water transparency, pH, and inorganic dissolved nitrogen ($R^2_{adjusted}=0.45$; $p<0.05$). The equation to summarize these relationships is described by

$$\ln CYN = 13 - 0.71 \ln WT - 3.5 pH + 0.29 \ln DO - 0.19 \ln IDN,$$

where

CYN Cyanobacteria density
WT Water transparency
DO Dissolved oxygen
IDN Inorganic dissolved nitrogen.

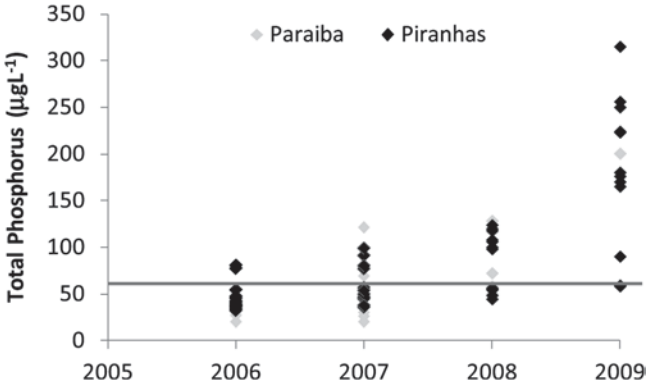

Fig. 5.10 Evolution of increasing phosphorus concentrations from 2006 to 2009 in the Paraíba River Basin

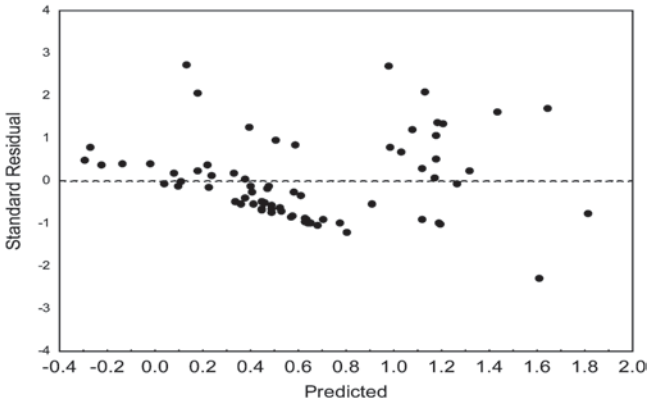

Fig. 5.12 Dispersion of the predicted values as a function of the residual pattern

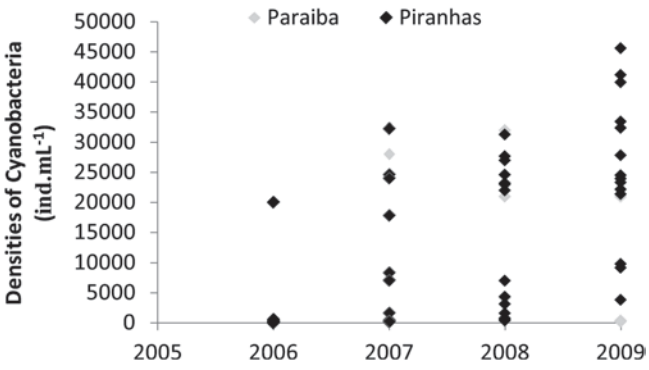

Fig. 5.11 Occurrence of cyanobacteria blooms in the Paraíba River Basins and the evolution of cyanobacteria densities from 2006 to 2010

The proposed model to describe the cyanobacteria density in the reservoirs was found to have residuals with a normal distribution ($W = 0.96$; $p = 0.73$) by the analysis assumptions (Fig. 5.12).

The availability of phosphorus has been regarded as one of the most important factors for determining phytoplankton biomass and water quality in lakes and temperate wetlands (Dilon and Rigler 1974) of tropical and subtropical regions (Attayde and Bozelli 1999; Huzart et al. 2006). However, reservoirs have different characteristics than natural lakes. For example, they often have unique morphology and hydrodynamics, as well as high loading rates of nutrients from the sediments and the drainage basin (Wetzel 1990). Thus, the driving factors of limnological dynamics are not likely to be similar in lakes and reservoirs, and therefore, the system responses to nutrient enrichment are likely to be different (Tundisi et al. 1990).

Our models demonstrated that cyanobacteria blooms, which are a regular problem in Brazilian semiarid reservoirs (Vasconcelos et al. 2011), did not have a direct relationship with phosphorus concentrations. This result suggests that phosphorus concentrations were not a good indicator of the trophic level of these reservoirs. The low transparency of the water was owing to high concentrations of suspend solids, which favors the growth of cyanobacteria while inhibiting other classes of phytoplankton.

The high suspended solids concentrations may have been influenced by an increase of aquaculture activities in the Brazilian semiarid reservoirs. The practice of farming fish in net cages is an important factor related to the elevated concentrations of nutrients and Chla, as well as a reduction of water transparency. The impact of fish farming on reservoirs is readily observable from the visible release of dissolved or suspended materials and metabolites from food remains (Starling et al. 2002; Lazzaro et al. 2003; Guo et al. 2009; Borges et al. 2010). These substances are associated with a high temperature, which favors an increase in the density of phytoplankton, and particularly cyanobacteria (Padisák 1997; Chorus and Bartram 1999; Reynolds et al. 1997), which may explain the high densities of cyanobacteria observed in the studied reservoirs.

Additional factors should be considered to help explain eutrophication in semiarid waters. Throughout the study period, the concentrations of TP and densities of cyanobacteria were clearly increasing. This can be explained by the increasing level of anthropogenic activities in the area and by the climatic features of the region. The long time necessary for water renewal is an important natural event that can maximize this problem. In addition to the low rainfall, other factors also influenced the eutrophication, including nutrient loads from tributaries during the rainy periods; furthermore, because renewal requires large inputs of relatively clean water, which did not occur during this period, the trophic levels of the reservoirs will likely be maintained or even worsen over time.

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Lake Eutrophication and Plankton Food Webs

6

Karl E. Havens

Abstract

The plankton food web comprises microscopic organisms that transport carbon and energy from producers to consumers in the water column of aquatic ecosystems. In lakes, the food web includes bacteria, phytoplankton, protozoa, micro- and macrozooplankton, and the trophic links between them. Structure of the plankton food web in lakes is affected in a predictable manner by eutrophication: phytoplankton biomass becomes relatively greater, while macrozooplankton biomass declines. The relative biomass of protozoa also may increase. Food web function also is affected: ecological transfer efficiency is lowest in ultraoligotrophic lakes and hypereutrophic lakes and highest in mesotrophic lakes. The relationship between the size of producers and grazers drives this unimodal pattern. In ultraoligotrophic lakes, cooccurrence of picoplankton with copepods that cannot directly graze such small particles results in long, energetically inefficient food webs with multiple steps including protozoa and microzooplankton. In hypereutrophic lakes, similar food webs occur, but owing to cooccurrence of cyanobacteria and small macrozooplankton that cannot handle those large and sometimes toxic phytoplankton. The dominance of large cyanobacteria in hypereutrophic lakes can be directly linked to enrichment with nutrients, particularly nitrogen and phosphorus, while the small size of zooplankton is attributed most often to intense fish predation. Long-term studies indicate that the changes in plankton food web structure and function can be reversed if nutrient loads are substantially reduced.

Keywords

Eutrophication · Plankton food web · Lake management · Fish · Plants

6.1 Introduction

Thousands of lakes around the world have been impacted by excessive inputs of nutrients from human-related uses of the land, and as a result have experienced changes in their ecological structure and function. This phenomenon, cultural eutrophication, is most often owing to an overenrichment of lakes with phosphorus (P) and/or nitrogen (N; Conley et al. 2009) and recent evidence suggests that its symptoms may be exacerbated by climate change (Moss et al. 2011) making the rehabilitation of culturally eutrophic lakes an even greater challenge in the future. One impact of eutrophication on lakes is a change in the structure and function of their food webs. The aim of this chapter is to provide a concise overview of how cultural eutrophication affects plankton food webs, drawing on research from the 1960s through studies completed in recent years. The chapter is divided into the

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following sections: a description of the plankton food web; an evaluation of data regarding how biomass distribution among components of the plankton food web changes along a gradient from nutrient-poor to nutrient-rich lakes; a consideration of how changes in the structure of plankton food webs affects their function in regard to their ability to effectively transfer energy to fish and other biota at higher trophic levels; a brief discussion of how other changes in the lake ecosystem influence how the plankton food web responds to eutrophication; and implications for the management of culturally eutrophic lakes.

6.2 The Plankton Food Web

Limnologists' view of the plankton food web has changed considerably since the mid-1900s when it was considered as a chain where phytoplankton fixed carbon that was then transferred directly to zooplankton and then to fish and other predators. This traditional view was supplemented by the concept of additional microbial pathways in the 1980s (Azam et al. 1983) and it is now widely recognized that bacteria and protozoa also play an important role in energy transfer and nutrient cycling in the plankton. Five major components and nine major links characterize the contemporary model of the plankton food web (Fig. 6.1). Phytoplankton fix carbon by photosynthesis and are consumed by a variety of different types of protozoa (including ciliates and flagellates) by microzooplankton such as rotifers and immature stages (nauplii) of copepods, and by macrozooplankton (cladocerans and copepods). A second route of energy flow occurs from protozoa to microzooplankton and macrozooplankton. Bacteria metabolize organic carbon that enters the lake from outside sources as well as carbon excreted into the water by phytoplankton, protozoa, and zooplankton. Bacteria are a food source for protozoa, microzooplankton, and macrozooplankton.

The Dashed arrows in Fig. 6.1 roughly correspond to energy flows in the traditionally recognized grazing food chain links in the web and the solid arrows to the microbial food web links. Although quantitative evidence regarding the importance of microbial links emerged in the 1980s (Azam et al. 1983; Sherr et al. 1987; Porter et al. 1988), their importance was conceptually identified by Lindeman (1942) who developed an energy flow diagram that included bacteria and links to and from phytoplankton, zooplankton, and dissolved materials. Gliwicz (1969) first speculated that the importance of microbial links may increase with eutrophication, a prediction that was proven to be correct based on results of later studies (Munawar et al. 2011).

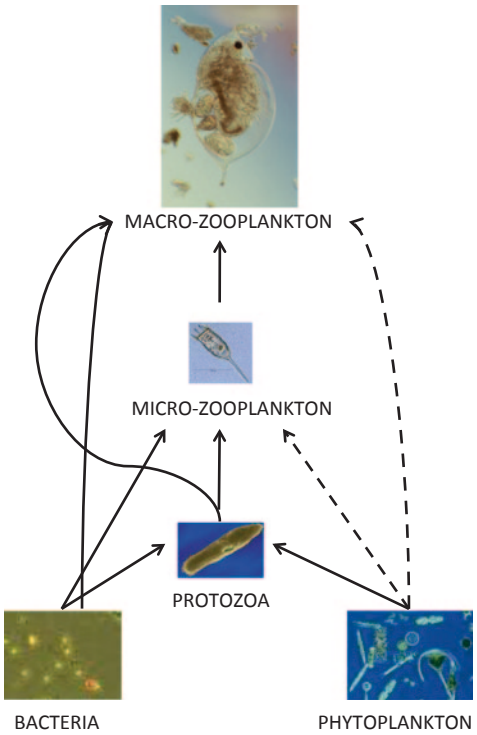

Fig. 6.1 A diagram of the plankton food web showing major components and links between them. *Solid arrows* correspond to links in the traditional grazing food chain and *dashed arrows* correspond to links in the microbial food web. Numerous species comprise each of the components shown here—individual species are shown as examples only

6.3 The Structure of Plankton Food Webs Versus Eutrophication

One typical and highly visible symptom of cultural eutrophication is increased biomass and dominance of large inedible cyanobacteria (e.g., Smith et al. 2006). Coincidentally, there are changes in the biomass and composition of zooplankton—including a loss of large species of *Daphnia*, and increased dominance of small rotifers and copepods (Weisse and Stockner 1992; Havens et al. 1996). Auer et al. (2004) performed a comprehensive analysis of plankton food web structure along a eutrophication gradient, comparing plankton communities in 55 lakes in northern Germany that ranged from mesotrophic to hypereutrophic. All the components of the food web displayed an increase in their biomass with greater levels of enrichment, indexed by chlorophyll concentration, although the rates of increase varied (Fig. 6.2). As a result, the proportional biomass changed: mesotrophic lakes had about 30 % of the plankton biomass in zooplankton and about 45 % in phytoplankton (Fig. 6.3a). Lesser amounts of biomass occurred in bacteria, heterotrophic flagellates, and ciliates. Over the gradient of enrichment, relative biomass of zooplankton dropped, to a low of around 15 % in

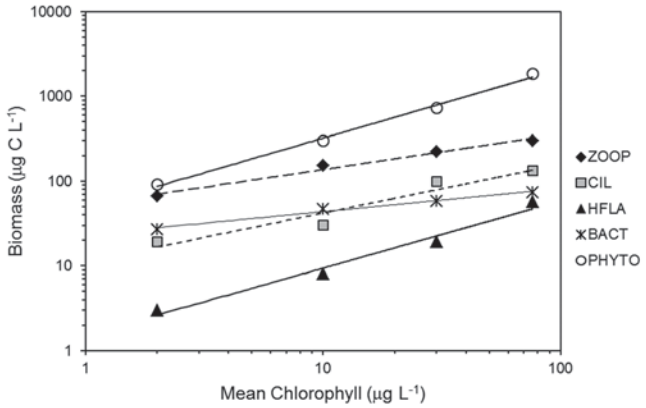

Fig. 6.2 Changes in biomass of zooplankton (ZOOP), ciliates (CIL), heterotrophic flagellates (HFLA), bacteria (BACT), and phytoplankton (PHYTO) observed by Auer et al. (2004) in a survey of German lakes. The *lines* are least square regression lines fit to the data points in order to illustrate the relative trends in these attributes

hypereutrophic lakes, while relative biomass of phytoplankton increased to a high of around 80%. Phytoplankton also increased in biomass relative to bacteria (Fig. 6.3b) and the percentage of protozoan consumers increased compared with metazoan consumers (Fig. 6.3c). Among the phytoplankton, there was a substantial increase in relative biomass of cyanobacteria, from less than 10% in mesotrophic lakes to around 65% in hypereutrophic lakes. This is similar to what was found in other studies (Downing et al. 2001). When Jeppesen et al. (2000a) examined data from 25 shallow lakes in New Zealand with total phosphorus (TP) concentrations ranging from 6 to over 600 mg l^{-1}, they found that with increasing TP there was an increase in ciliates, a decrease in macrozooplankton density (especially *Daphnia*), and reduced zooplankton size. Jeppesen et al. (2005) documented that these changes can be reversed; based on data from lakes around the world, substantive reduction of external nutrient loads could quickly (within 10 to 15 years) result in a return of *Daphnia*, increased macrozooplankton density and size, and reduced phytoplankton biomass.

Results from the subtropics are comparable with some exceptions. Havens et al. (2007) examined data from Lake Okeechobee, a large eutrophic lake in Florida, USA, in the same manner as was done by Auer et al. (2004) in Germany. Compared with the temperate lakes bracketing its level of nutrient enrichment, Okeechobee had a higher relative biomass of ciliates and grazing by protozoa was twofold as important

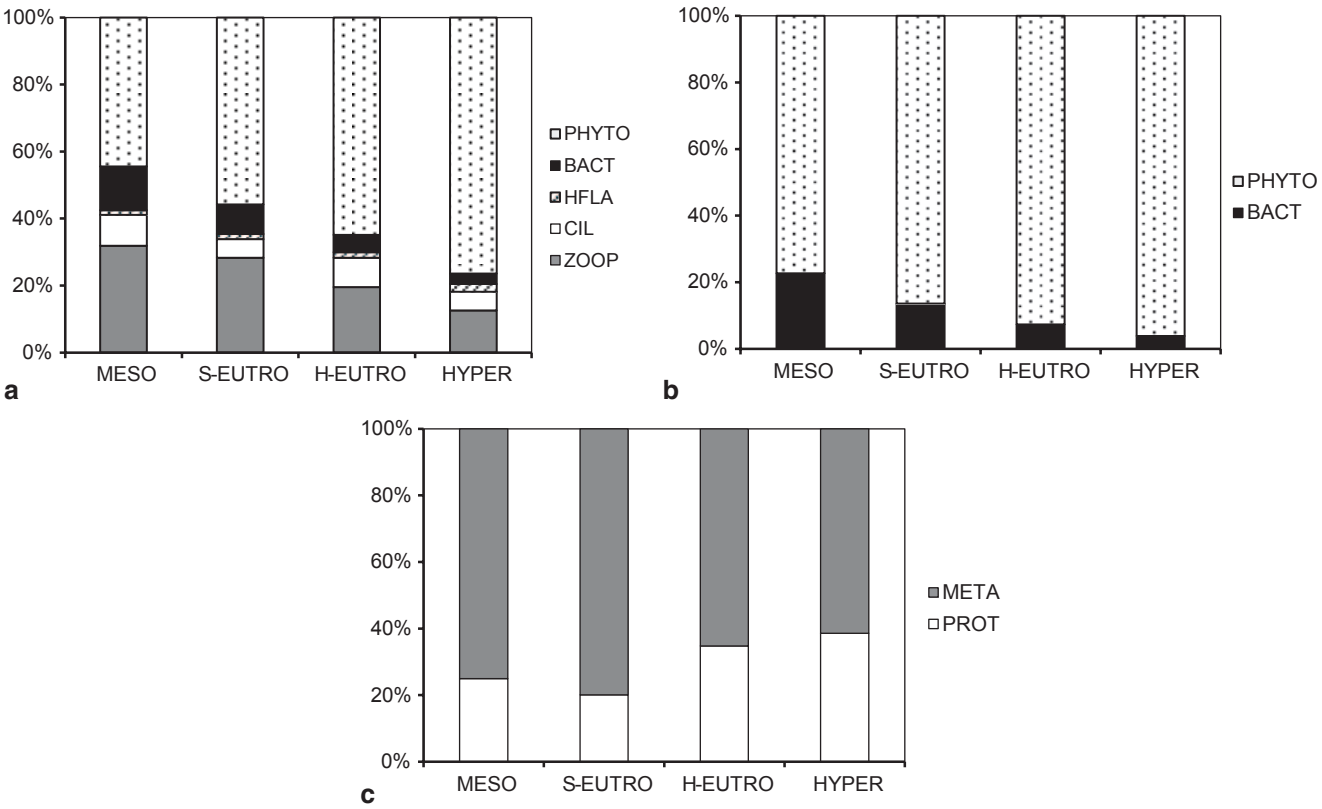

Fig. 6.3 Differences in the relative biomass of various plankton groups (**a**), including phytoplankton (PHYTO), bacteria (BACT), heterotrophic flagellates (HFLA), ciliates (CIL), and zooplankton (ZOOP) in German lakes differing in trophic state including mesotrophic lakes (MESO), slightly eutrophic lakes (S-EUTRO), highly eutrophic lakes (H-EUTRO), and hypereutrophic lakes (HYPER); differences in relative biomass of phytoplankton versus bacteria in those lakes (**b**); and differences in metazoan (META) versus protozoan (PROT) grazers in those lakes (**c**). The figures were developed based on data from Auer et al. (2004)

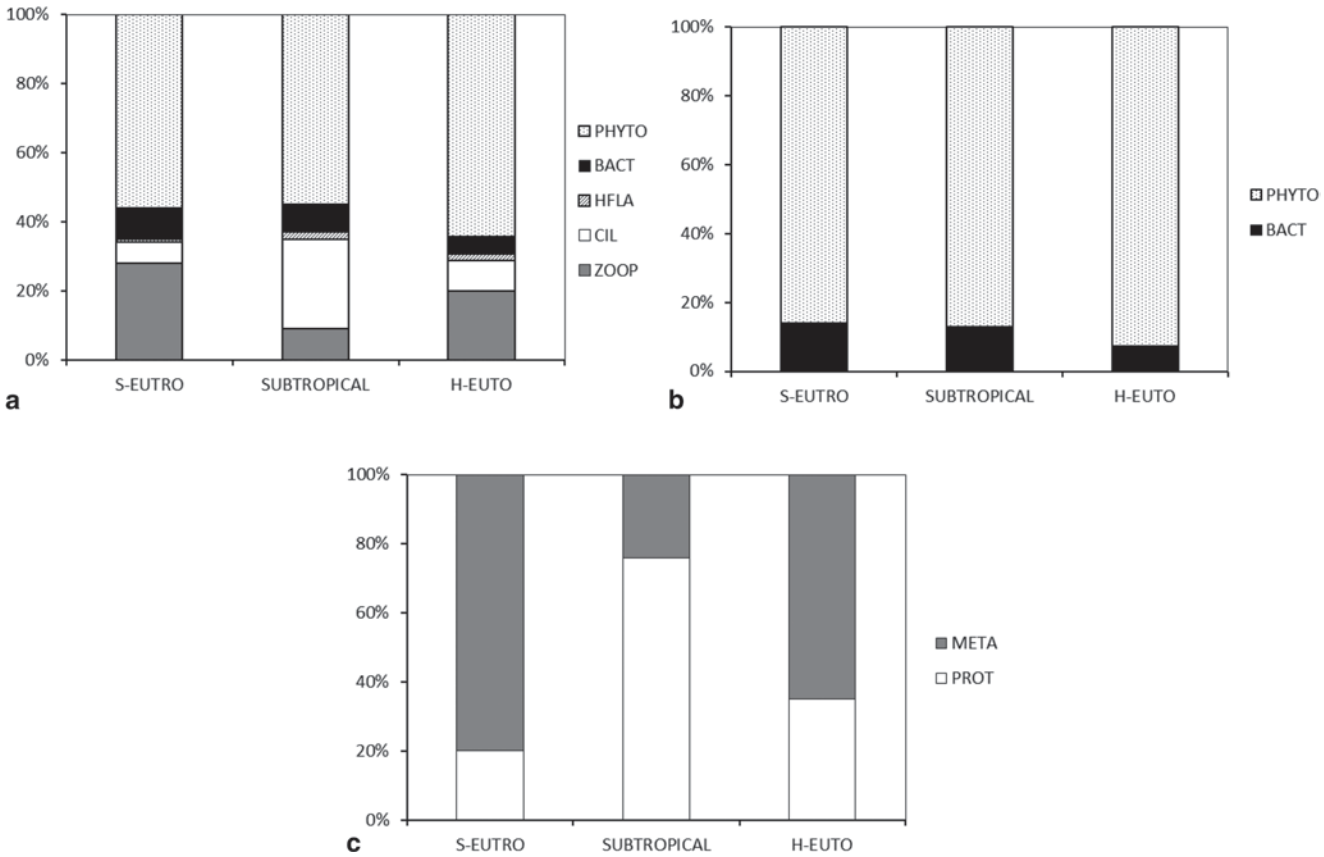

Fig. 6.4 A comparison of the relative biomass of various plankton groups shown in Fig. 6.3, comparing a subtropical lake to slightly eutrophic and highly eutrophic German lakes that bracket its trophic state (**a**); the same comparison, looking at relative biomass of phytoplankton versus bacteria (**b**); and the same comparison, looking at the relative biomass of metazoan and protozoan consumers (**c**). The figures are developed based on data from Auer et al. (2004) and Havens et al. (2007)

(Fig. 6.4). On the other hand, the relative biomass of bacteria and phytoplankton were comparable. The difference in protozoa grazing reinforced an earlier finding that the microbial food web is of particular importance in eutrophic lakes of the subtropics (Crisman and Beaver 1990). A quantitative food web diagram for Lake Okeechobee (Fig. 6.5) illustrates the typical situation observed in eutrophic subtropical lakes with a high biomass of phytoplankton (mostly cyanobacteria) and relatively low biomass of macrozooplankton.

6.4 The Functioning of Plankton Food Webs Versus Eutrophication

Hillbricht-Ilkowska (1977) first identified that across an enrichment gradient from oligotrophic to eutrophic lakes there is a unimodal curve of energy transfer efficiency in the plankton food web—with peak efficiency occurring in mesotrophic lakes. This result can be explained on the basis of size of predominant phytoplankton and zooplankton. In ultraoligotrophic lakes, picophytoplankton coexists with copepods that are not able to directly graze the tiny (1–2 μm) phytoplankton because their filtering structures are not fine enough to effectively capture them. Thus, in ultraoligotrophic lakes, energy transfer to copepods involves multiple steps in an elongated food web, from picophytoplankton to protozoa to microzooplankton and finally to macrozooplankton (Stockner and Shortreed 1989). At each step, some energy is lost to respiration, so the relative amount reaching the top of the web (and available to fish) is low. In large numbers of these nutrient-poor lakes, fisheries managers have intentionally added nutrients in order to stimulate algal productivity, increase the size of dominant algal species, and create food webs with direct connections between producers and zooplankton grazers (Stockner and MacIsaac 1998).

In stark contrast to this situation, mesotrophic lakes predominantly have a highly efficient one-step food chain (Fig. 6.6a) with relatively edible phytoplankton and large *Daphnia* (Weisse and Stockner 1992), an animal known to be the most effective grazer among zooplankton both in regard

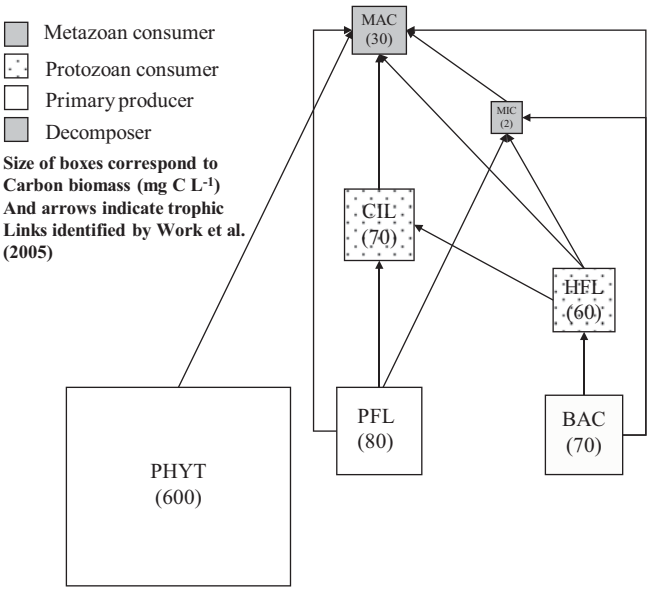

Fig. 6.5 Partitioning of carbon among various components of the plankton food web of a subtropical eutrophic lake, Lake Okeechobee, Florida. The data are based on Havens et al. (2007). *MAC* macrozooplankton, *MIC* microzooplankton, *CIL* ciliates, *HFL* heterotrophic flagellates, *PFL* phototrophic flagellates, *BAC* bacteria, *PHYT* phytoplankton

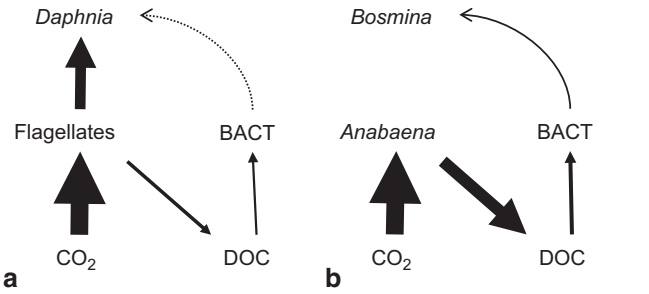

Fig. 6.6 Simple diagrams of C flow in food webs contrasting dominance of *Daphnia* and edible flagellates (**a**) with dominance by *Bosmina* and inedible cyanobacteria (**b**). The *thickness of arrows* corresponds to relative amounts of C flow

to its quantity of grazing and wide size range of grazed particles. In hypereutrophic lakes, size again interferes with direct energy transfer in the grazing chain. Large cyanobacteria such as *Anabaena* coexist with small zooplankton such as *Bosmina* that cannot eat those phytoplankton (Fig. 6.6b). The cyanobacteria excrete carbon that is taken up by bacteria and then is routed up through a microbial web to the zooplankton.

Quantitative data documenting the unimodal pattern in food web efficiency were presented by Jeppesen et al. (2003) based on a comprehensive survey of 466 lakes spanning the temperate to arctic zones and encompassing a broad range of trophic states. Other studies documenting the predominance of a microbial food web in eutrophic lakes include Riemann and Sondergaard (1986), who compared the plankton in two lakes differing in degree of nutrient enrichment, and Cole et al. (1988), who compared the plankton in 24 lakes across an eutrophication gradient.

Because complex food webs lead to greater energy loss compared with one-step chains where *Daphnia* directly graze phytoplankton, eutrophication-induced changes in food web efficiency have implications for higher trophic levels. At some point, the upward flow of energy may become insufficient to support an additional trophic level, such as piscivorous fish (Persson et al. 1988). Havens et al. (2000) documented the low ecological transfer efficiency that is typical of highly eutrophic lakes. They measured transfer efficiency of plankton when cyanobacteria dominated the phytoplankton and copepods dominated the zooplankton using a radiotracer method developed by Ducklow et al. (1986). Havens et al. (2000) inoculated whole water samples including indigenous plankton with ^{14}C-labeled glucose or bicarbonate (carbon sources for bacteria and phytoplankton, respectively). In both cases, they found that just 0.1% to 1.0% of the carbon was transferred to >200 m size particles (macrozooplankton) after 4 h of incubation. The same results were obtained when the experiment was repeated four more times over a year-long period. Similarly, when Sommaruga (1995) developed a carbon budget for a eutrophic lake in Uruguay dominated by filamentous cyanobacteria and small zooplankton, they measured extreme low ecological transfer efficiencies. This situation may explain, in part, why it is common to find hypereutrophic lakes dominated by fish, such as gizzard shad and carp, which can feed low in the food web, i.e., graze directly on phytoplankton and detritus (Bays and Crisman 1983; Allen et al. 2000), and thereby circumvent the inefficient plankton food web.

6.5 Changes in Plants and Effects on Plankton

Other profound changes, described in this book, occur in lakes as they undergo eutrophication, and some of them can affect the plankton food web. One notable change is the loss of submerged aquatic vegetation (SAV) when biomass of cyanobacteria becomes extremely high in the phytoplankton. Cyanobacteria blooms block light penetration to the extent that they shade out the SAV. The phenomenon is most common in shallow eutrophic lakes and it has been suggested that it can happen quickly, with a lake quickly transitioning from a clear water phase with abundant SAV and low phytoplankton biomass and a turbid water phase with little or no SAV and high phytoplankton biomass as the lake crosses a nutrient threshold (Scheffer et al. 1993). When SAV is lost from a lake, so too is the refuge they provide for *Daphnia*

and other large zooplankton against plankton-eating fish, or refuge for those fish against larger fish predators. Depending on the role that the plants were playing in the particular lake, loss of SAV could lead to a reduction or increase in the zooplankton. It should be noted that there is some debate as to whether the rapid switch from clear to turbid is typical or unusual. Sayer et al. (2010), for example, studied SAV and phytoplankton dynamics in 39 shallow lakes in the UK and Denmark over a broad nutrient gradient. They documented a long-term loss of SAV in many lakes that were affected by cultural eutrophication and suggested that there was a gradual replacement of plants by phytoplankton over a time period of 10 to 100 years, rather than the sudden switch predicted by the alternative states model. Other recent studies support this view (e.g., James et al. 2005). Yet, there are cases where transitions happen more quickly. In Lake Okeechobee, Florida, for example, we observed a switch from turbid water with dense cyanobacteria blooms to clear water with widespread SAV (*Chara*) in just 1 month (Havens et al. 2001). To a large extent, the rate of change may depend on the bottom morphology. In the case of Lake Okeechobee, the switch happened across a large area of shallow water with a nearly flat bottom versus the gradually sloping shoreline that is common in many lakes.

6.6 Changes in Fish and Effects on Plankton

Changes in fish assemblages also occur with eutrophication and this may be owing, in part, to the afore-mentioned changes in the plankton food web; similarly, fish may have strong top-down impacts on the plankton. In particular, shallow eutrophic lakes support high densities of planktivorous and omnivorous fish (Jeppesen et al. 2007) including species that are voracious sight-feeding predators of zooplankton, as well as filter-feeding omnivores such as gizzard shad that consume benthos, phytoplankton, and zooplankton (Crisman and Beaver 1990). Warm-water lakes in the subtropics appear to have particularly high predation pressure on the zooplankton and have extreme low ratios of zooplankton to phytoplankton biomass, absence of *Daphnia* (e.g., Jeppesen et al. 2007; Havens et al. 2009), and lack of control of the phytoplankton by zooplankton grazers (Havens et al. 1996). In these lakes, most energy flow happens in microbial pathways (Crisman and Beaver 1990; Work et al. 2005).

Although some (e.g., Hart 2011) suggest that large inedible phytoplankton are responsible for these characteristics, most research indicates that the paucity of zooplankton is a direct response to fish predation (Meerhoff et al. 2007; Iglesias et al. 2008; Jeppesen et al. 2007; Havens and Beaver 2012). Jeppesen et al. (2000a) documented that in New Zealand lakes, there is a strong positive correlation between fish and phytoplankton biomass, but no such correlation between zooplankton and phytoplankton. These results indicate top-down control of the zooplankton by fish predation. Jeppesen et al. (2003) also examined data from 466 temperate to arctic lakes and found a strong pattern: fish control over large zooplankton is strongest in oligotrophic and highly eutrophic lakes and weakest in mesotrophic lakes (consistent with the findings about unimodal relationships discussed earlier). Jeppesen et al. (2000b) found that across a TP gradient of <50 to >400 g l^{-1}, there was a decline in piscivores, an increase in cyprinids, a shift to smaller zooplankton, and a reduction in mean body weight of cladocerans from 5.1 to 1.5 g. The ratio of zooplankton to phytoplankton biomass dropped from 0.5 to 0.1 as biomass of phytoplankton increased 15-fold. In three lakes where fish kills occurred, the trends in plankton size and biomass quickly reversed, similar to the findings noted earlier in lakes that underwent reductions in external nutrient loads. Similarly, Auer et al. (2004) found that increases in rotifers, ciliates, and nanoflagellates seen in hypereutrophic lakes occur because of relaxed grazing pressure by larger Cladocera, which have been eliminated by fish. In Lake Okechobee, Florida, we recently found that seasonal changes in the ratio of zooplankton to phytoplankton biomass are almost entirely driven by seasonal changes in biomass of the zooplankton and that those changes coincide with periods of high versus reduced fish predation.

6.7 Implications for Lake Management

Reduction of external nutrient loads is a prerequisite for reversing cultural eutrophication. At the same time, the process may be hastened if it is possible to perform some ecological engineering of the food web. This sometimes is done by manipulating the density of planktivorous or omnivorous fish in order to reduce grazing pressure on *Daphnia*, so that animal can become more abundant and graze down the phytoplankton (e.g., Shapiro and Wright 1984; Carpenter et al. 1987). The goal is to reduce the amount of phytoplankton per unit of P in the lake, via an animal that can filter large volumes of water and feed on nearly the entire plankton food web, from phytoplankton to bacteria. The challenge is maintaining the lowered biomass of planktivorous and omnivorous fish. At some point in the rehabilitation process, where the lake reestablishes an oxygenated deep water zone in summer, it may be possible to introduce piscivorous fish to naturally keep planktivores under control. These approaches are not as effective in the subtropics, where large *Daphnia* generally do not occur, and where the microbial food web is more important than in temperate lakes of a similar degree of enrichment (Crisman and Beaver 1990; Havens et al. 2007). Thus, in the subtropics, control of external nutrient loading

is of greater importance for reversal of eutrophication. Although this situation is now restricted to the subtropics, with global warming, the same challenges could migrate northward into temperate lakes (Moss et al. 2011).

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Environmental Impacts of Tourism on Lakes

7

Martin T. Dokulil

Abstract

Ecosystem services are the benefits provided to people by ecosystems and biodiversity. Fresh water is a 'provisioning' service referring to the human use of fresh water for several purposes. The hydrological cycle also sustains inland water ecosystems, including rivers, lakes and wetlands. These ecosystems provide regulating, supporting and cultural services that contribute directly and indirectly to human well-being through recreation, scenic values and fisheries. To maintain ecosystem health or ecosystem integrity, external or internal perturbations must be kept below the carrying capacity.

Anthropogenic disturbances of freshwater resources as a consequence of tourism are diverse. In many regions of the world, lakes and ponds in particular are important freshwater habitats providing significant attraction for the public. Impacts to lakes from tourist activities occur directly to the lake water and shoreline, or can affect the water body indirectly through various actions in the catchment. The response of a specific freshwater ecosystem depends on the type of interference as well as the type and size of the lake. Shallow lakes are affected and hence behave differently from deep lakes. Large lakes react in a different way than small lakes. Impacts are also modified and mediated by the characteristics of the catchment, such as morphology, size, land-use and population structure.

Impacts to tourist lakes are classified as direct and indirect effects and are analysed and exemplified.

Keywords

Ecosystem service · Eutrophication · Recreation · Water quality

7.1 Introduction

The human population benefits from a multitude of resources and processes that are supplied by natural ecosystems. These benefits are collectively known as ecosystem services. Fresh water as a water resource is a 'provisioning' service referring to the human use of fresh water and includes products like pure drinking water or clean water for recreation. In the near future, global change will alter the supply of ecosystem services that are so vital for us (Schröter et al. 2005).

Anthropogenic disturbances of freshwater resources as a consequence of tourism are very diverse. Lakes and ponds are particular important freshwater habitats providing significant attraction for the public. The intention of this review is to compile and summarize touristic impacts on lakes of any size.

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7.2 Environmental Impacts of Tourism

The quality of the environment, both natural and man-made, is essential to tourism. The relation between tourism and the environment is complex—many activities can have adverse environmental effects. Many of these impacts are linked with the construction of general infrastructure such as roads and airports, and of tourism facilities, including resorts, hotels, restaurants, shops, golf courses and marinas. The negative impacts of tourism development can gradually destroy the environmental resources on which it depends. On the other hand, tourism has the potential to create beneficial effects on the environment by contributing to environmental protection and conservation. It is a way to raise awareness of environmental values and it can serve as a tool to finance protection of natural areas and increase their economic importance. This branch called ecotourism is rapidly expanding.

Negative impacts from tourism occur when the level of visitor use is greater than the environment's ability to cope with this use within the acceptable limits of change. Uncontrolled conventional tourism poses potential threats to many natural areas around the world. It can put enormous pressure on an area and lead to impacts such as: soil erosion, increased pollution, discharges into the sea, natural habitat loss, increased pressure on endangered species and heightened vulnerability to forest fires. It often puts a strain on water resources, and it can force local populations to compete for the use of critical resources.

7.3 Water Resources and Tourism

A lake that is suitable for tourism must:

- Be easily accessible.
- Have the necessary infrastructure.
- Have warm water surface temperature preferably >20 °C.
- Have good water quality ('clean water').

The best category to comply with these criteria is an oligo-mesotrophic lake.

The tourism industry generally overuses water resources for hotels, swimming pools and personal use of water by tourists. This can result in water shortage and degradation of water supplies as well as generating a greater volume of waste water. Moreover, tourists have a tendency to consume more water when on holiday than they do at home. The amount used can be up to 440 L a day. This is almost twice as much what the inhabitant of an average city uses. Particularly in drier regions, water scarcity is then of particular concern.

Recreational activities of tourists on lakes are summarized together with their possible consequences and effects in Table 7.1. The relations between the entities in Table 7.1 are not meant, however, as being 1:1. One form of utilization may have several consequences resulting in a number of effects. Swimming, for instance, may cause eutrophication and contamination, which in turn can lead to increased nutrient load, reduced oxygen concentration and finally algal blooms.

Shallow lakes are usually more vulnerable to disturbances than deep lakes. Lakes that thermally stratify during summer act as nutrient sinks with no or little re-suspension. Internal nutrient load therefore is often negligible. In contrary, shallow lakes do not thermally stratify, nutrients are not permanently buried and re-suspension is common, which may lead to high internal loading. Short-term weather events and diurnal changes are more pronounced in shallower lakes compared with deep lakes. Morphometry, water level change and flushing are of much greater importance when lakes are moderately deep. The littoral zone and the aquatic vegetation are usually more significant for shallow ecosystems. These and other factors are summarized in Dokulil et al. (2012).

Off all the consequences mentioned in Table 7.1, eutrophication most severely affects water quality and hence lake tourism. Because of its importance, it is also one of the best studied impacts on lakes worldwide. The critical loading concept developed by Vollenweider (1976) and extended by Vollenweider and Kerekes (1982) works sufficiently well in most types of lakes (e.g. Dokulil and Teubner 2003, 2011). In shallow lakes, which are turbid or dominated by submerged macrophytes, however, chlorophyll concentrations often tend to be considerably smaller than predicted from total phosphorus (TP) because much of the phosphorus is unavailable (Dokulil et al. 2006). In such cases, restoration efforts can be made successful by applying bistable theory (Dokulil et al. 2006, 2011).

Disturbances by tourists impact not only the lake but also the shoreline, the watershed (catchment) including the ground water and even the airshed (atmosphere). The dimension of the impact in each category depends on a number of parameters describing the entity and diminishes the further one moves away from the water body. Effects on the lake depend on the size (large or small), depth (deep or shallow) and type (natural, constructed or urban).

Impacts affecting the shoreline are dependent on the nature of the shore (rocky, stony or sandy). In addition, the aquatic as well as the terrestrial vegetation, the structural diversity and the degree of modifications are important.

The areal size of the catchment in relation to lake area, the flat or mountainous morphology and the land-use primarily determine the loading to the lake. The degree of urbanization and the location relative to the lake in the watershed can influence lakes in many ways through population density and activity of residents and tourists.

Effects from the airshed can originate from the economic activity and population density of a wider region because of long-distance atmospheric transport under the influence of

Table 7.1 Summary of lake utilizations in touristic areas leading to various consequences and effects

Utilization	Consequences	Effects
Recreation	Eutrophication	Algal blooms
Swimming	Pollution	Reduced O_2 concentration
Angling	Littering	Waterborne diseases
Boating	Contamination	Fish kills
Water sports	Erosion	External/internal nutrient load
Scuba diving	Disturbances	Shore erosion
Shoreline activities	Noise pollution	Diffuse run-off
Watershed activities	Gas emissions	Vegetation destruction

The entities in the Table are not meant as 1:1 relations
See text for further explanation

Table 7.2 Overview on potential direct and indirect impacts by touristic activities on lakes

Direct impacts	Indirect impacts
Chemicals liberated from skin	Nutrient load from catchment
Nutrient release and input	Increase of internal load
Bacterial contamination	Chemical pollution through run-off
Sediment re-suspension	Waste and storm water input
Wave effects	Floodwater increase
Damage of water plants	Macrophyte removal
Alien species introduction	Water level changes
Changes in fish composition	Water abstraction (from lake and groundwater)
Waste dumping	Land-use change in the catchment (industrialization, vegetation change)
Shoreline constructions (housing, jetties and marinas buoys)	Increased urbanization
Littering	Soil sealing
Shoreline destruction	Gas emissions to the atmosphere
Shoreline vegetation change	Disturbance of wildlife
Disturbance of wildlife	Reduction in biodiversity
Fish farming	

weather conditions. All these impacts can further be differentiated into direct and indirect disturbances (Table 7.2).

7.4 Impacts on Lakes

Touristic impacts on lakes usually come from a number of recreational activities. The most important ones are swimming, boating and angling. These impacts will be discussed in the following sections.

7.4.1 Swimming

Swimming is usually positively linked with fitness and well-being. Risks associated with swimming in a lake come from turbidity, currents, pollution or pathogens contained in the water. These risks are commonly seen as ecosystem threats. Rarely, the people recognize that the swimmers themselves produce these risks when large numbers are involved, as in public beaches or pools.

Health problems largely originate from bacteria such as coliform bacteria, *Escherichia coli*, fecal streptococci, *Pseudomonas aeruginosa* as well as yeasts and fungi originating from swimmers, introduced by water birds or carried in through waste water discharged into the lake.

Ecological problems mainly come from the input of nutrients such as phosphorus and nitrogen either washed off from the skin or emitted via urine. On average, each swimmer or bather contributes 0.094 g P per day to the water body (Schulz 1981). According to Binder (1994), the critical phosphorus load should not exceed 0.07 g P m^{-2} a^{-1} for shallow lakes that are less than 5 m deep. Nutrient accumulation leads to increased turbidity due to enhanced algal growth, which can create pH problems and finally cumulate in algal blooms. These deteriorations can affect bathers. Turbidity reduces visibility thus increasing accident risks while hindering rescue operations. Certain algal types, particularly cya-

Table 7.3 Impacts, effects, potential risks and their significance resulting from angling and related activities. Modified from Lewin et al. (2006)

Example	Effects	Risks	Significance
Exploitation	Catch decline population fluctuations	Population collapse, decrease in genetic diversity	***
Size selectivity	Changes in length and age distribution	Truncation of natural age structure	***
Species selectivity	Selective removal of species	Alteration in species composition, changes in trophic cascade, loss of resilience	***
Stocking Transfer of (bait) fish	Negative impacts on local fish stocks owing to competition, predation, hybridization or diseases, non-indigenous species introduction	Native species decrease or are lost, fish communities change, ecosystem changes occur	***
Sex selectivity	Vulnerability of either males or females to angling	Effective population size decreases, effects on recruitment	**
Bye-catchcatch and release	Injuries and stress in species	Mortality immediate or delayed Sub-lethal fitness impacts	**
Nutrient input	Negative impacts on water quality	Eutrophication, water quality deterioration	**
Loss of angling gear	Damage to wildlife	Survival and fitness of birds Risks to humans	*
Disturbance of habitats and wildlife	Macrophyte damage, impacts on water birds	Loss of habitats, stress and reduced recruitment in birds	*
Boat traffic and noise	Wave action, emissions, stress	Negative impacts on littoral vegetation and on survival and fitness, decrease in water quality	*

nobacterial species can produce toxins, which are released into the water. Skin irritation or even allergic reactions in sensitive individuals are then possible. Algal blooms washed on shore create aesthetic problems not only by looking ugly but also because of the smell produced during decay.

7.4.2 Angling

Exploitation and impacts from angling have received much less attention compared with commercial fishing. Over the last decades, inland commercial fisheries strongly declined in economic importance in the industrialized countries while angling became increasingly more important particularly for tourism development. This is even true for the developing countries, where fishing is still important for subsistence (Cowx 2002a, b).

Although the management of recreational fishing has regionally received considerable attention, the dimension of angling and the potential impacts of fishing on fish populations and aquatic ecosystems are largely underestimated. A single angler may have a low or moderate impact on fish stock. It is, however, the cumulative impacts large numbers of anglers can induce which matter. Since angling is usually practiced during leisure time, it becomes increasingly important for tourism. Recently, Lewin et al. (2006) have extensively documented and discussed the potential impacts of non-commercial recreational fishing, angling and associated activities. Their main results are summarized in the following paragraph and in (Table 7.3).

The most severe impacts from angling are exploitation of fish stock, size and species selectivity. Exploitation rates can be highly variable ranging from less than 10% to over 80% depending on fish species. Among many other factors, rates also depend on the angling effort, which in turn is affected by local regulations particularly, the fishing period duration. Effects of exploitation can be compensated by fish stocking, which can be a major impact of the fishery on aquatic ecosystems. In addition, fish are often deliberately or accidentally introduced. The introduction of non-indigenous or alien fish species can have considerable long-term and widespread ecological and biological effects on native fish stocks.

Through their selectivity for fish species and size, anglers can be seen as keystone predators adding a further trophic level on aquatic ecosystems. Depending on the fish species targeted, angling can severely affect the trophic cascade. For a more detailed discussion, refer to the review by Lewin et al. (2006).

Activities related to angling can disturb littoral habitats through boating or near-shore trampling. Additional effects originate from wave action, noise and nutrient input (Table 7.3). The loss of fishing gear may seem unimportant but can, e.g. severely affect birds. A good example is provided by Pühringer (2011).

7.4.3 Boating

Any boat may interact with the aquatic ecosystem and disturb habitats but the major effects come from motorized watercraft such as commercial tourist boats, power boats or fishing boats. Personal watercrafts such as jet skis add additional effects (see http://ww.pwia.org/UserFiles/File/History-PWC.pdf). Effects of boating on aquatic systems are extensively discussed by Asplund (2000) and are briefly summarized here.

Boats have direct and indirect effects on a number of lake water, littoral and shoreline parameters. Water clarity

Table 7.4 Summary of potential mechanisms by boating on aquatic ecosystems and their effects. Modified from Asplund (2000)

	Emissions Exhaust	Propeller Hull contact	Turbulence	Waves Wake	Noise	Movement
Water Clarity		■	■	■		
Water Quality	■					
Shoreline erosion				■		
Macrophytes		■	■	■		
Fish	■	■	■			■
Wildlife		■		■	■	■
Human enjoyment	■			■	■	■

Shaded areas indicate potential effects

is affected by an increase in turbidity, nutrients or algal biomass. According to Yousef et al. (1980), waves generated by motorboat propellers increased phosphorus on average by 28–55 %. Maximum increase in turbidity was observed shortly after boating activity but remained high for almost 25 h. Sediment re-suspension, higher turbidity and larger TP concentrations tended to be greater in shallower lakes than deeper lakes (Asplund 1996).

Fuel leakage and emissions affect water quality by adding metals, hydrocarbons and other pollutants to the water. According to Wagner (1991), who provides a good review on the subject, toxic effects on aquatic organisms are in general minimal because amounts are usually small and hydrocarbons are highly volatile. However, polyaromatic hydrocarbons and fuel additives may have effects on drinking water supply. Moreover, accumulation in sediments in certain places, e.g. near marinas might be a problem for water organisms.

Wakes and waves produced by boats can be up to 40–50 cm depending on the size and speed. These waves can severely increase shoreline erosion (e.g. Johnson 1994) and may also indirectly affect submerged and emergent aquatic macrophytes through their movement but also through increased turbidity. Plant communities are more susceptible to direct effects from boat hulls or propellers (e.g. Asplund and Cook 1997).

Boats have very little direct effect on fish, fish breeding or fish behaviour. Of much greater importance are the indirect effects through the disturbance of fish habitats (Lagler et al. 1950). Similarly, wildlife is indirectly disturbed by the destruction of habitats and deterioration of water quality. Direct effects of boating on wildlife are noise and direct contact with propellers (Asplund 2000). Moreover, effects on human enjoyment, which disturbs peace and quiet, air quality, safety and crowding should not be under-estimated.

A further aspect of boating is the number of boats permitted on a lake because the effects on lakes mentioned earlier are cumulative and related to the quantity of boats. There is, however, very little scientific evidence on this aspect (Anthony and Downing 2003; Beachler and Hill 2003; Burger 2003). On Neusiedler See, a large shallow lake in Austria, for example, cumulative boat days for the period May to September 2004 to 2006 have increased from 488 to 584 with peaks occurring mainly on weekends and an ever-increasing tendency (Fig. 7.1).

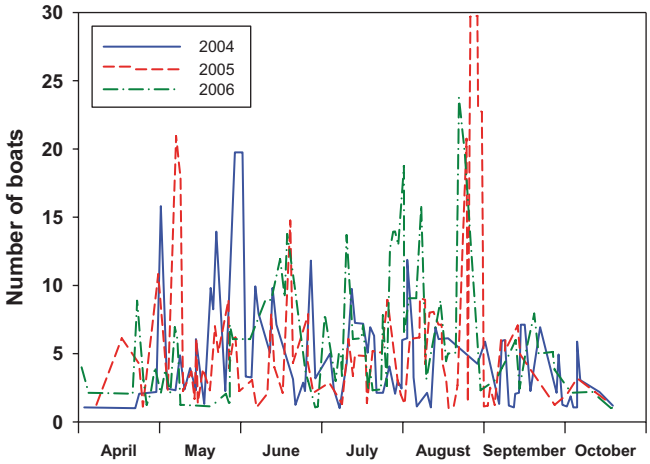

Fig. 7.1 Number of boats on Neusiedler See in the period April to October of each year from 2004 to 2006 (Herzig, personal communication)

7.4.4 Impacts on the Shoreline

Shore zones are characterized by the type of substrate, vegetation, slope and structural diversity. The zonation of the vegetation and the definitions are elegantly summarized in Fig. 7.2 reproduced here from Ostendorp et al. (2004). Shorelines are under pressure by a wide variety of human activities in the immediate lakeshore and remotely in the catchment. Recreation and tourism have direct impacts through facilities and increased numbers of holiday makers resulting in habitat destruction, trampling, littering and disturbance of breeding birds or sensitive mammals.

The degree of modification and the accessibility of the shoreline is an important aspect. In developed regions of

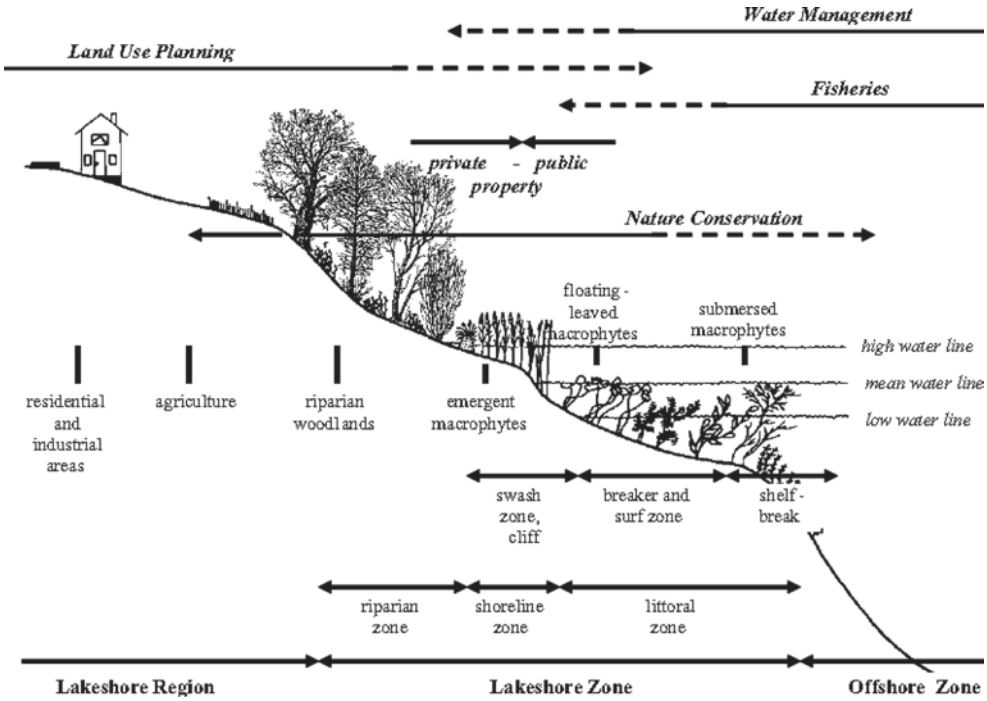

Fig. 7.2 Definitions and zonations of the lakeshore and littoral zone. Reproduced from Ostendorp et al. (2004)

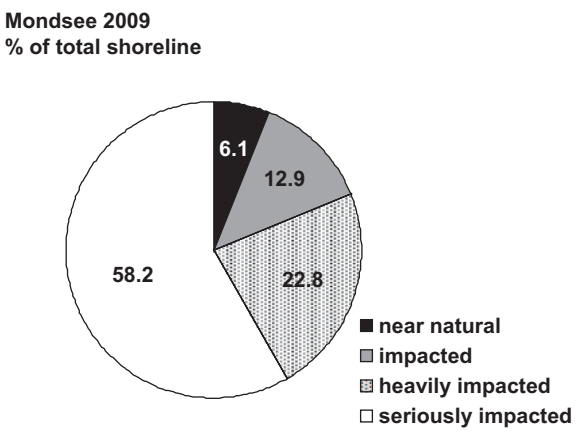

Fig. 7.3 Percentage of lakeshore modification in Mondsee 2008. Modified from Ritterbusch-Nauwerck (2011)

the world, only small fractions of the total shoreline are in a more or less natural state. A recent analysis of shoreline modification on Mondsee, a deep, touristic pre-alpine lake in the Salzkammergut region of Austria reveals that only 6.1 % of the lakeshore is in a near-natural state and more than 50 % is seriously impacted or inaccessible (Fig. 7.3).

7.4.5 Impacts from the Catchment

Any tourist-related activities in the catchment, such as new apartments, holiday villages, sport centres, clearings for ski slopes and land-use changes, will ultimately have some sort of indirect influence on the receiving lake. At the landscape scale, physical processes such as orography and the size of the catchments contribute to their character and hydrology, influencing ecosystem functions such as water capture, water storage or floodwater detention (Everard et al. 2009). All these functions and their associated ecosystem services respond to climate change (Tucker and Slingerland 1997).

Eutrophication, primarily from diffuse sources, is a particular problem originating in the drainage basin. Relevant parameters are land-use and their intensity precipitation, population density, nutrient emission and nutrient retention. Associated with these factors is the degree of soil erosion from the catchment. For the receiving lake or lakes in the drainage basin, their landscape position, connectivity to other water bodies or wetlands as well as the lake network complexity is important (Martin and Soranno 2006). Moreover, as climate changes, extreme events in the drainage basin become increasingly important for nutrient transport and loading (e.g. Zessner et al. 2005; Strauss and Staudinger 2007). Recently, more holistic approaches have been used to evaluate pressures including tourism on trans-boundary lake districts (Klug 2010).

7.4.6 Impacts from the Airshed

Similar to the disturbances from the drainage basin, impacts arise from long-distance transport of air pollutants in the airshed. These pollutants can originate to some extent from tourist-related activities and may significantly influence lakes. Most notable is the acidification problem created

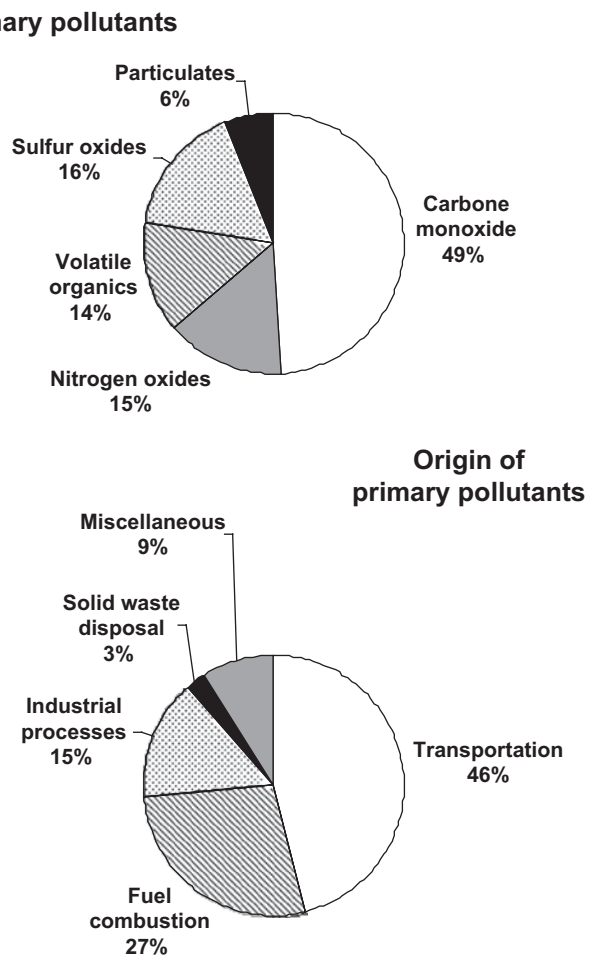

Fig. 7.4 Relative proportion of gaseous primary pollutants and their origin

mainly by gaseous emissions from fuel burning and exhausts from cars. Depending on many factors, in particular the geology of the catchment, acidification by primary pollutants (Fig. 7.4) or secondary pollutants produced in the atmosphere primarily decreases the pH values in streams, rivers and lakes. As a consequence, a multitude of complex direct and indirect effects occur in freshwater biological systems (D'Itri 1982).

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Eutrophication in the Great Lakes of the Chinese Pacific Drainage Basin: Changes, Trends, and Management

8

William Y. B. Chang

Abstract

China has 25 of the world's great lakes (> 500 km^2). This number of great lakes is exceeded only by Canada and Russia. Tectonic uplift and fluvial actions are the primary mechanisms resulting in the formation of these lakes. Long-term climate changes have significant impacts on these lakes, especially in terms of: (1) lake size and depth and (2) chemical characteristics. In recent years, the increased temperature has also led to the onset of the blue-green alga *Microsysti* in the Pacific Drainage Basin (PDB). Over the most recent 40 years, human activities have had a visible effect on the large lakes situated in the human-dominated PDB. Large lakes in this basin have become depositories of agricultural, industrial, and household wastes and have shown an increased level of eutrophication and toxic chemical accumulation. These great lakes have changed from oligotrophic in the 1960s, to eutrophic in the 1980s, and to hypereutrophic in the 1990s, with increased occurrence of blue-green *Microsysti* blooms. These blooms have become serious concerns for water supplies and the health of people and aquatic ecosystems.

Continuing disposal of untreated domestic and industrial wastes has contributed to this change. Lake management practices, such as dams and weirs for flood control and extensive use of littoral area and wetland for farming, aquaculture, and home construction, have also contributed to the acceleration of this process.

With its enormous population and increasing use of large lakes, China needs to integrate its lake management programs and to plan for sustainable use of its aquatic resources. The management plan should take into consideration the environmental costs of development and the ecological service that the lakes provide. The reduction or recycling of wastes by industries needs to be closely controlled. The involvement of average citizens in decisions in environmental planning and lake management is another key to the success of managing these important water bodies.

Keywords

Eutrophication · Great lakes · Water quality · Management

8.1 Introduction

China is the most populous country in the world and ranks third in territory. Lakes account for more than 80,000 km^2. It has 25 of the world's great lakes with a total area reaching over 30,000 km^2. These lakes have been used extensively

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Table 8.1 The number and total area in each lake size category (Academia 1981; Chang 1987)

Lake size (km^2)	Number	Total area (km^2)
1–10	2,383	9,129
10–50	234	4,932
50–100	107	7,365
100–500	96	19,830
500–1,000	14	9,213
>1,000	11	27,629
Total	2,845	78,098

and play an important role in flood control, fishing and aquacultural production, supplying drinking and irrigation water, transportation, and recreation. Large increases in urbanization over the last 40 years and accelerated industrial development since the 1980s have greatly extended the uses of the great lake environment in the Pacific Drainage Basin (PDB). Under the market-based economy, such uses have rapidly changed lake physical environments and increased the complexity of managing these aquatic environments (Chang 1993, 1996). This chapter reports on trends and changes at the five great lakes situated in the PDB and the current challenges being faced in the management of these lakes.

8.2 Distribution, Origins, and General Characteristics

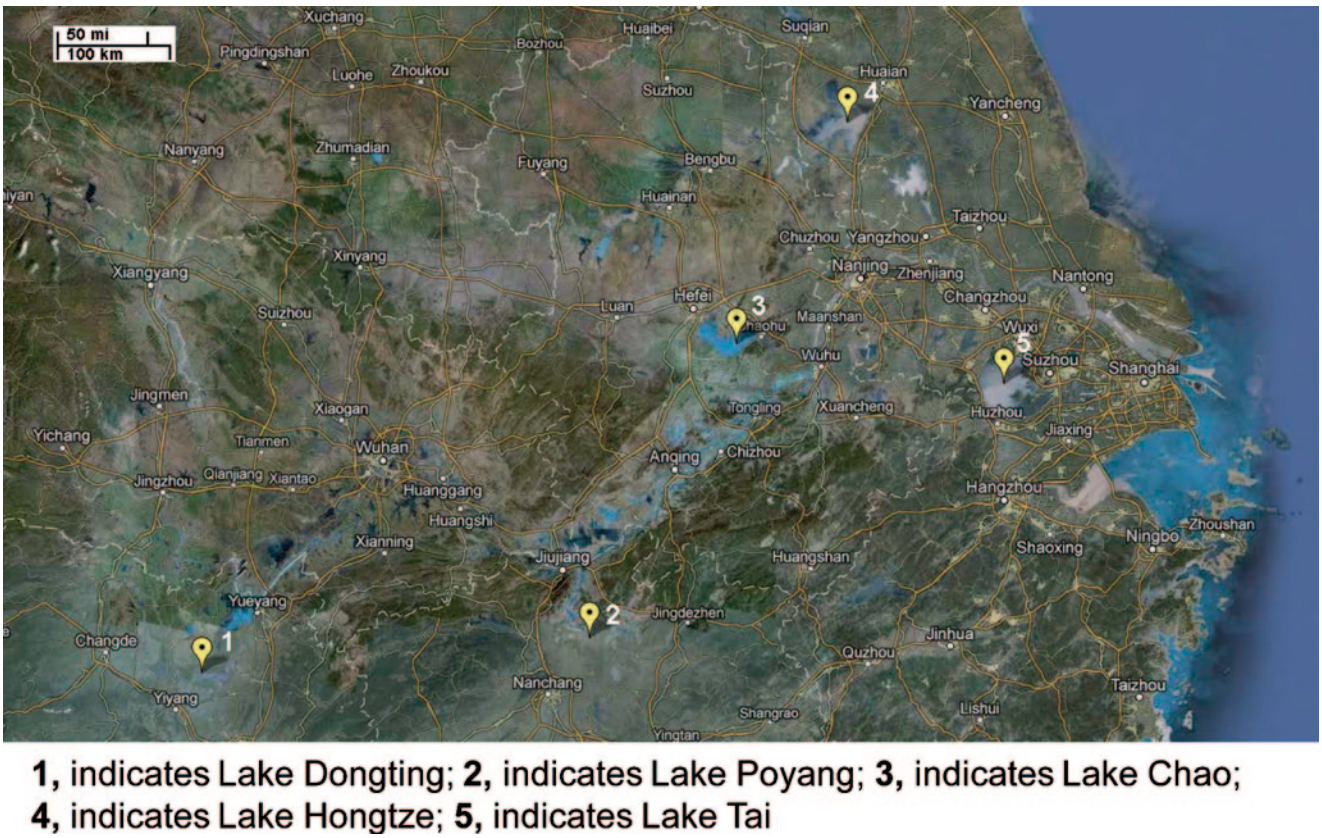
China has more than 2,800 lakes larger than 1 km^2 occupying approximately 80,000 km^2 (Table 8.1) and constituting approximately 0.8% of the entire national territory. Twenty-five are among the world's great lakes (>500 km^2) with a total area of 36,842 km^2 representing 47.2% of the total national lake area. Lakes from 1–10 km^2 are the most numerous, numbering more than 2,000 and covering a total area of 9,000 km^2 (11.6% lake area; Table 8.1). Of the Chinese great lakes, five are situated in the PDB; these lakes are facing increasing anthropogenic pressure. This chapter focuses on these five great freshwater lakes: Lakes Chao, Dongting, Poyang, and Tai in the Yangtze Basin and Lake Hongtze in the Huai River Basin (Fig. 8.1). These lakes are not only in the PDB, but also are close to major urban centers. They provide water supplies to the surrounding cities and receive both the household and industrial wastes from these cities.

Tectonic movement and river action are two major mechanisms contributing to the formation of great lakes in China. The great lakes situated in the PDB are primarily a result of river action. They are shallow and eutrophic. Changes in river courses (primarily that of the Yellow River) and river sediment deposits were the major factors leading to the formation of lakes in the Yangtze River Drainage Basin and the Huai River Drainage Basin. When the Yellow River changed its course between 1194 and 1845 A.D. to run along the old course of the Huai River as it drained into the sea, large amounts of sediment were deposited at the mouth of the Huai River. Eventually, these deposits blocked access to the sea. The Yellow River pushed out yet another outlet to the sea, while the sediment blocking the Huai River Basin gave rise to a series of lakes. These include two great lakes (Lakes Chao and Hongtze) as well as many smaller lakes. Similarly, the sediments brought down by the Yangtze River and other rivers gave rise to Lakes Dongting and Poyang (Zhang and Chang 1994) and contributed to the formation of Lake Tai and of chains of small lakes in the Yangtze River Delta area in Jiangsu Province. These riverine lakes are shallow and eutrophic and have been used for food production, waste disposal, flood control, transportation, irrigation, and recreation. These lakes are surrounded by urban centers and are closely related to the daily life of the people. They have been used extensively by people in the PDB, which is the home of more than 95% of the Chinese population.

8.2.1 Hydrology

River inputs and precipitation are the primary means of replenishing water to the large lakes in China's PDB. Seasonal monsoons and melting snow are two major water sources. The moisture brought by the seasonal monsoon is the principal source of water for the large lakes situated in the PDB. The Yangtze and Huai Rivers are the major water carriers to these large lakes. Precipitation directly onto the lake surface constitutes a relatively small percentage of the total input of water (<5%; Academia 1981; Shi et al. 1989). Annual evaporation is generally balanced by annual precipitation onto the lakes in the PDB. The major water output is by way of river outflow.

In the PDB, high lake levels correspond with the monsoonal rains in June, July, and August. Fluctuations in both water level and size can be over 10 m in riverine lakes, which drain directly into the Yangtze River. In riverine lakes, such as Lakes Dongting and Poyang, the annual fluctuations in levels are 13.6 and 7.3 m, respectively. The size of these lakes also varies greatly with seasons. For example, Dongting Lake varies in size from 2,740 to 12,000 km^2, depending on time of year. The extent of fluctuation in water level and size has been found to be related to the catchment basin and lake surface ratio. Lake Dongting has a ratio of 86.6:1 and Lake Poyang has a value of 46.1:1 (the catchment basin of the Yangtze River is not included in these statistics; Academia 1981; Shi et al. 1989). In contrast, the value for both Lakes Chao and Tai is 16:1, while the water level differences are only 2.5 and 1.3 m, respectively. Because lakes such as Dongting and Poyang have no embankments and dams, they not only fluctuate greatly in size and water level, but also have much greater water exchange rates (flushing rates). For example, the flushing rate for Lake Dongting is 13 days, while that for Lake Tai is 263 days.



1, indicates Lake Dongting; **2,** indicates Lake Poyang; **3,** indicates Lake Chao; **4,** indicates Lake Hongtze; **5,** indicates Lake Tai

Fig. 8.1 Map of five great lakes in China

The result of these differences is that although the amounts of nutrient input loads to these lakes are similar, effects in term of eutrophication in these lakes are different. Lake Dongting has remained eutrophic, while Lakes Chao and Tai, with more limited water exchanges, are now hypereutrophic.

8.2.2 Water Quality Trends

Changes in water quality in the lakes in the PDB have been particularly noticeable during the most recent 40 years, as large increases in urbanization along these lakes and accelerated industrial development in the lakes' watershed have increased urban and agricultural run-off to the lakes. These changes have made water quality a top environmental concern in China. In general, population levels in a lake watershed are a good first approximation for determining the level of the lake's eutrophication. The higher the population density, the greater the likelihood that serious pollution and water quality problems are found (Chang 1993). Water quality is deteriorating in most lakes close to urban centers (Shu 1991). Large lakes such as Lakes Tai and Chao are hypereutrophic and are the final destination of sewage and industrial wastes from the surrounding urban centers (Yang et al. 2008).

The change in water quality in Lake Tai is a case in point. Anthropogenic inputs to the lake have been increasing since 1950, as population and human activities in the immediate watershed of the lake have increased. However, the rate of the change was slow in the 1960s and 1970s, the types of the inputs during those periods were primarily agricultural and household wastes, and the amounts involved were relatively low. Strong currents provided vigorous water circulation in the lake and a relatively high dissolved oxygen (DO) level. During the 1970s, the DO level was greater than 7 ppm, even at the bottom of the lake. During the 1960s, Lake Tai was generally oligotrophic (Table 8.2), with inputs of primary organic matter from the immediate watershed.

Untreated effluents from the watershed draining into Tai Lake have increased substantially over the last 30 years. The total amount of untreated effluents was estimated in 1987 at 33.83×10^6 tons per year (Chang 1996). This amount has increased substantially, primarily from small chemical and manufacturing plants close to Lake Tai. This untreated effluent rapidly began to change the degree of eutrophication in Lake Tai and affected the water quality of the lake. Table 8.2 shows the average concentration of nitrogen (N) and total phosphate in 1960, 1980, and 1988. The eutrophication thresholds of phosphorus (P) for freshwaters are from 0.02 to 0.10 mg P L^{-1} and of N are from 0.500 to 1.00 mg N L^{-1} (Lin et al. 2008; Xu et al. 2010). In 1960, Lake Tai was categorized as oligotrophic;

Table 8.2 Changes in nutrient concentrations in Lake Tai between 1960 and 1988. (Adapted from Sun and Huang 1993)

	1960	1980–1981	1987–1988
No3-n (mg L^{-1})	0.02 (0.01–0.09)	0.75 (0.60–1.15)	0.95 (0.01–5.80)
Nh3-n (mg L^{-1})	0.02 (0.01–0.03)	0.12 (0.01–0.22)	0.19 (0.01–3.87)
Tin (mg L^{-1})	0.05	0.89	1.16
Top (mg L^{-1})		0.006	0.022 (0–0.56)
Tp (mg L^{-1})	0.02		0.032 (0–0.61)
Phytoplankton counts (Cells L^{-1})	19,240	10,116,000	38,170,000

The values in the parentheses are the minimum and maximum values measured in milligram per liter
TIN total inorganic nitrogen, *TOP* total organic phosphate, *TP* total phosphate

total inorganic nitrogen (TIN) in the lake was only 0.05 mg N L^{-1}, SRP was 0.02 mg P L^{-1}. By 1981, TIN had increased to 0.89 mg N L^{-1} and SRP remained stable (Table 8.2). In 1988, TIN and TN concentrations were 1.12 and 1.84 mg N L^{-1}, respectively, and total phosphorus (TP) was 0.032 mg P L^{-1} (Sun and Huang 1993). However, by the end of year 1988, TIN and TN concentrations had increased to 1.58 and 2.34 mg N L^{-1}, whereas TP was 0.085 mg P L^{-1} (Qin et al. 2007). Increases of more than one order of magnitude were seen in total N concentrations and total phosphate between 1960 and 1988. As the lake became more eutrophic, seasonal changes in nutrient concentrations also became greater. The concentrations of TIN and TP change inversely with the dry and wet periods. By 1988, TIN and TP concentrations were three times higher during the low water dry period than during the high water wet period (Sun and Huang 1993). Many areas in the lake showed the effects of advanced culture eutrophication during the dry period, while eutrophic conditions improved during the wet period. The highest nutrient concentration was usually found in March, before the onset of the monsoon rains, while the lowest in situ concentration was in September at the end of the monsoon period (Sun and Huang 1993). Precipitation in this case plays a significant role in water quality conditions in this lake. The rate of increase in TP and TN continued; TP increased from 32 μg L^{-1} in 1987–1988 to 108 μg L^{-1} in 2001–2003, while TN increased from 1,160 μg L^{-1} from 1987–1988 to 1,771 μg L^{-1} in 2001–2003.

8.2.3 Phytoplankton

More than 125 genera of algae have been reported from the large lakes in the PDB (Nanjing Institute of Geography 1982). Of these 125 genera, the diatoms contribute a major proportion of the total assemblage in all seasons; in some lakes, however, spring and sometimes autumn have relatively higher diatom assemblages. Lack of clear seasonal diatom cycles may be a result of the absence of a seasonal thermocline, since lakes are shallow and diel vertical mixing occurs whenever wind is strong, and nutrients from sediments are resuspended in the water column. The diatom assemblages of sheltered bays and open waters have been found to differ substantially from each other in forms and numbers.

The green algae are also a key group of phytoplankton, but are transitory species. The population density peaks in spring and decreases in summer. Blooms are found on the surface of shelter bays and in the littoral zone of large lakes.

The blue-greens appear late spring and bloom in summer when the temperature is high in these lakes. The blooms occur in the lakes where the flushing rate is slow and where nutrient inputs are high, such as Lakes Tai, Cao, and Hongtze. The blooms are often found on the surface of the water and comprise *Mycrocystis* and *Anabaena.* Regional climate changes in recent years appear to be catalyzing the algal surge by raising average water surface temperatures and increasing water column stratification, leading to more bloom of blue-greens, and especially of the blue-green alga *Mycrsystis aeruginosa*. The blue-greens produce toxins that can damage the liver, intestines, and nervous system. Blue-green blooms in Lakes Tai and Chao are becoming annual occurrences and they threaten drinking water supplies and sustainability of freshwater ecosystems (Stone 2011).

The steep increase in TP and TIN concentrations after 1980 is the result of the use of N-P-K fertilizers in the catchment basin and of receiving industrial waste effluents from nearby chemical factories. In the last 30 years, small manufacturing plants have sprung up as part of the Chinese economic revolution that made the Yangtze River Delta part of a global factory. Most of these factories have no water treatment equipment and use the lakes for waste water disposal. As a case in point, in 1987 there were 3,000 factories in the Lake Chao Basin; only 2.5 % of effluents were treated, and this lake received 140 million ton of industrial effluents annually (Jin et al. 1990). The N concentration in the lake increased more than 20-fold from 1963 to 1984 and the blue-green algae and diatoms increased 3.15- and 2.47-fold, respectively (Jin et al. 1990). There are only a very limited number of waste water treatment plants; moreover, the number following appropriate operational guidelines is even smaller. The amount of effluents to this and other lakes have not been abated. The same phenomena are observed in all five of these great lakes, all of which are receiving increasing amounts of the waste

Table 8.3 Large lakes in the human-dominated Pacific drainage basin and their TP, TN, and chlorophylla-a. (Adapted from Chang 1996)

Lake names	Lake area (km^2)	TP (ug L^{-1})	TN (ug L^{-1})	Chlorophylla-*a* (ug L^{-1})
Chao (Hyper-Eu)	770	192.5	3,035.0	15.67
Dongting (Eu) riverine lake	2,433	44.0	1,087.0	3.9
Hongtze (Hyper/Eu)	2,069			
Poyang (Eu) riverine lake	2,933	47.0	617.0	2.65
Tai (Hyper-Eu)	2,425	108	1,771.0	7.89

Hyper-Eu hypereutrophic, *Eu* eutrophic

Table 8.4 Phytoplankton biomass, percentage, and major species. (Adapted from Sun and Huang 1993)

Algal group	Biomass (mg^{-1})	%	Dominant taxa
Blue-Greens	2.76	37	*Microcystisaeruginosa*
			Chroococus
Cryptomonas	1.81	25	*Cryptomonaserosa*
Diatoms	1.58	22	*Melosiragranulata*
			Navicula
			Cyclotella

effluents. Lakes Dongting and Poyang are, however, blessed by their high flushing rates. Owing to their low water retention rates, the waste effluents enter the Yangtze River and then flow into the East China Sea. The TPs for these lakes are under 50 μg L^{-1} (Table 8.3). In contrast, Lake Cao has 192 and 3,035 μg L^{-1} of TP and TN, respectively, while Lake Tai's TP and TN are 108 and 1,771 μg L^{-1}, based on a survey conducted in 2001–2003 (Table 8.3).

Yang et al. (2008), based on their survey of the lakes in the Yangtze floodplain, reported that a TP concentration of 80–110 μg L^{-1} is a critical range for a shift from epiphytic diatom taxa to planktonic species, because the latter are more tolerant of turbid waters and high nutrient concentrations. They noted a similar trend for the transformation from macrophyte-dominated systems to algal-dominated systems. Jeppesen et al. (1990) also found a similar switch if the critical TP ranges are 80–150 μg L^{-1} in lakes in Denmark. Following this trend, macrophytes in Lake Tai lose ground to algae beginning in 1990. Scientists at the Chinese Academy of Science have now reintroduced cultivated macrophytes in Lake Tai, by curtaining off sections of the lake and seeding them with macropytes. The plants have flourished in the experimental areas, but outside that area, they have failed because the water is too polluted.

In response to substantial increases in nutrient enrichment, the phytoplankton assemblages in the lake have also changed greatly since 1960. Species diversity has been decreasing since 1960 and the lake is currently dominated by a few species with exceedingly high abundance. Phytoplankton counts in 1960, 1980, and 1988 showed a geometrical increase (Table 8.4). The predominant algal groups found in the 1988 lake samples are the blue-greens, the crytomonas, and the diatoms; the biomass, percentage, and dominant species in each of these groups in 1988 is shown in Table 8.4. The dominant taxa of phytoplankton found in Lake Tai are the forms most commonly appearing in eutrophic waters.

Control of N, P, or availability of both controls phytoplankton growth. It is generally accepted that N is the prime limiting nutrient in marine systems, whereas P is the prime limiting nutrient in freshwater systems. Xu et al. (2010) reported that the eutrophication threshold of P for freshwaters is from 0.02 to 0.10 mg P L^{-1}, and that of N is from 0.50 to 1 mg N L^{-1}. They used the N concentration at the onset of blooms of the toxin-producing cyanobacteria *Microcystis spp*. in the summer of 1980 as a threshold for this spp. The onset N concentration was therefore determined at 0.8 mg NL^{-1}. Using this threshold N level and in situ bioassay, Paerl et al. (2011) and Xu et al. (2010) suggested that when P enrichment as >0.20 mg P L^{-1} and N enrichment >0.80 mg N L^{-1}, growth of *Microcystis spp.* is not nutrient-limited, and the availability of N during the summer is a key growth-limiting factor for the proliferation and maintenance of toxic *Microcystis spp.* blooms. N load reduction in this case is essential for controlling the magnitude and duration of blue-green blooms in Lake Tai.

8.3 Anthropogenic Impacts

More than 95% of the Chinese population has settled in the PDB. The population growth rate in this basin is also the highest in the country and the total basin population tripled within only 40 years, reaching 1.1 billion in 1991. This high

population density has sharply increased the need for lake resources and has multiplied the uses of lake environments (Chang 1990). These great lakes in this area not only serve as sources for drinking water, fish, and aquatic food production, but also play important roles in transportation, flood control, and waste disposal. In general, large lakes close to urban centers also receive disproportionately large amounts of household and industrial wastes. As a result, they have become increasingly eutrophic and have elevated concentrations of organic toxics, with frequent occurrence of cyanobacteria blooms.

The economic initiatives of the 1980s stimulated major industrial development resulting in a great increase in industrial effluents. Since industries were treating only about 25% of these effluents (even that amount is an optimistic estimate), most of the raw effluents, containing a large number of contaminants, have been draining into lakes. High levels of metals and toxic organics have already been found in lake sediments and benthic fishes in large lakes close to urban centers, such as Lakes Tai and Chao. These contaminants include mercury, arsenic, phenol, copper, cyanide, zinc, lead, and chromium, and can be readily associated with the nearby major industrial sources (Nanjing Institute of Geography 1982; Sun and Wu 1989; Sun and Huang 1993).

The economic initiatives that began in the 1980s also led to new sources of pollution from rural industry. Prior to the early 1980s, most major Chinese industries were situated in urban areas. The primary sources of industrial pollution were the industries in urban centers and this situation was known to local inhabitants. However, in the late 1980s, many rural industries sprouted up. These industries are usually operated by one or a few families and are spread throughout all rural communities in China. They are generally poorly equipped with little or no environmental treatment facilities. These rural industries have become a major source of toxic chemicals and have been responsible for the spread of these chemicals from primarily urban centers to many rural communities, which are experiencing increasing amounts and deadlier types of pollution. These rural industry sources have had an extensive impact on tributaries and lakes in many places quite far from previously known pollution sources.

Extensive use of the littoral areas of lakes for aquaculture and farming to increase the food production in China has led to an increase in eutrophication and is responsible for the substantial reduction in lake areas in the PDB. The rate of reduction in the size of the PDB great lakes is high. For example, increased use of wetland and littoral zones in Lake Tai beginning in the 1950s significantly reduced the lake size. The total area of the littoral zone converted to farmland and ponds between 1950 and 1980 was 160 km^2 (Sun and Huang 1993). The highest annual rate of conversion was during the 1970s.

The conversion of lake areas for rice and fish farming also had major ecological effects on Lake Tai (Chang 1996). This conversion reduced the area covered by aquatic vegetation, which is important to many littoral species for spawning, foraging, and protection during maturation. As a result, many species that depend on this environment have been declining, most notably fish species such as common carp *Cyprinus carpio* and crucian carp *Carassius auratus*. With the reduction in carp species, the families *Engraulidae* and *Salangidae*, which prefer open water and prey primarily on large zooplankton, have quickly become dominant in the lake. These opportunistic fish species are small in size (adults have an average size of 7–10 cm), with a short maturation period of about 1 year. Wong showed an inverse relationship between the population of fish species *Engraulidae* and *Salangidae* and the zooplankton population in the lake. A large increase in *Engraulidae* and *Salangidae* populations has had a major effect on the zooplankton population. The depressed zooplankton population, in turn, results in a relatively high density in the phytoplantkon population. The effects of littoral conversion have significantly changed the trophic dynamics and the fish population in Lake Tai. This could indirectly affect the effort to control unwanted algal blooms in that lake (Chang 1996).

The Chinese government has recognized the severe impacts of littoral conversions, which include the reduction of the floodwater holding capacity of the large lakes and significant changes in lake ecosystems. In 1980s, it announced a program of returning the farmland previously claimed from lakes to lake use. This program was only minimally successful since the trend of population growth and need to use this area for housing construction and urban expansion acted against it.

8.4 Lake Management

8.4.1 Institutional Arrangements

Management of Chinese lakes falls under several different authorities. The Ministry of Water Resources is responsible for flood controls and the construction of dams and weirs. The National Environmental Protection Administration (NEPA) has the authority for pollution regulation and for establishment of environmental laws related to lakes. The Ministry of Agriculture provides guidelines for managing fisheries and natural resources, which are primarily focused on increasing the production of fish and aquatic products. The daily management of lakes is, however, the responsibility of provincial, county, and township authorities. The level

of the local authority responsible for managing a lake depends on the lake's size, location, and ownership. A Lake Management Commission is usually established for lakes of significant economic importance. Because flood controls, environmental pollution, and the development and use of natural resources are directed by different agencies, the Lake Management Commissions play an important role in the coordination between these different agencies, accommodating various needs and uses. When this coordination is inefficient or fails, the signs of deterioration can often be seen at many lake sites.

The changes in eutrophication conditions in Lake Tai reflect a general trend of nutrient enrichment in large lakes in the PDB. Chinese authorities have realized the seriousness of halting this continuous deterioration in water quality and have established laws for controlling industrial effluents and provided funding to study eutrophication issues. A case in point is the action taken by NEPA, the major agency in China, dealing with environmental and water quality issues. This agency has conducted several national lake surveys to better understand the extent of lake pollution problems and has provided funds for treating eutrophication problems. Lake Tai has also received funds from NEPA for its water quality studies with additional funds from the Chinese Academy of Science, the Chinese Natural Science Foundation, and Jiangsu Province. In addition to these efforts, Lake Chao in Anhui Province has also received a sizable grant from NEPA and Anhui Province to study and improve lake water quality. However, water quality continues to worsen in the lakes in the PDB and many have developed seasonal or regional anoxic conditions.

In May 2007, an algae outbreak sparked by unusually hot weather overwhelmed a water filtration plant that supplies Wuxi City on Lake Tai's north shore, leaving more than 2 million people without drinking water for a week. This outbreak prompted Wuxi City and its Environmental Protection Bureau to take the unusual action of forcing hundreds of small chemical and manufacturing plants near Lake Tai to close or relocate. They instituted strict controls on effluents from the factories that were permitted to stay in order to cut down on pollution and the massive influx of N and P. These actions leveled off the continuing downturn of water quality conditions in that lake (Stone 2011).

Industries are the primary sources of lake pollution in the PDB since they contribute more than 75% of the total untreated run-off and have the greatest impact on lake quality. Industrial run-off also has the most severe impact on aquatic environments. Monitoring and controlling industrial pollution is NEPA's responsibility; NEPA issues guidelines for industrial effluents and assists the local EPA in monitoring run-off from factories. The day-to-day responsibility for monitoring and controlling industrial pollution, however, rests with the local EPA. The level of regional supervision of polluted industries depends on those factories' official classification. For example, the provincial EPA supervises the provincial industries, while the county EPA has authority with respect to county enterprises and factories. In general, the factories that have received national attention are monitored carefully and have installed pollution devices to meet the Chinese water quality standards. However, these factories are in the clear minority. Despite the creation of national and regional environmental agencies in China, the development of major environmental laws and the creation of an impressive network to enforce these regulations, most industrial wastes are not monitored and no routine lake survey has been carried out for most lakes. Furthermore, because many regional authorities (at both the county and municipal levels) lack sufficient operating revenues, regional EPAs rely heavily on the funds from pollution fines to operate. This dependency provides little incentive for regional authorities to control industrial pollution and to reduce industrial run-off. As a result, the decline of public waterways continues. Water quality in most lakes in the PDB faces further deterioration.

8.4.2 Flood Control

water resource management and flood control are the two major lake management activities carried out by the Ministry of Water Resources. In order to control floods and maximize the use of water resources, the Ministry of Water Resources and the regional water authorities have installed weirs and dams in most waterways and lake tributaries since the 1950s, except in those lakes, such as Lakes Poyang and Dongting, where the quantity of the water flowing in and out of the lakes is so large that controls are impractical. The management of water quantity and levels in lakes, and decisions regarding opening and closing dams, are the responsibility of water resources authorities. In most cases, the floodgates are raised in winter to drain lake water and provide the capacity needed to accommodate peak flow in spring and summer; floodgates are closed for most of the rest of the year. There is little or no water outflow in spring, summer, and fall except where lake water levels become unsafely high. The construction of dams and weirs since the 1950s has reduced potential damage to lowland areas in several major floods and has increased the use of lakes and waterways for other activities such as irrigation and transportation.

However, the construction of dams and weirs for flood control, while useful in other respects, has greatly affected fisheries resources and aquatic life, especially those species, which use riverine spawning grounds and live in the lakes. Recruitment of these species in most lakes is impossible as a result of dam construction and some carp and crab species have experienced noticeable population reduction. Fingerling and larval fish stocking programs are now the major

means of maintaining lake fish productivity in order to sustain lake fisheries. These dams and weirs have also reduced water exchange and have increased accumulation of urban and industrial wastes. Because of the large amount of wastes accumulated by these dams and weirs, their sudden annual opening often leads to anoxic and toxic conditions downstream and death of many aquatic species.

8.5 Lake Management Concerns

8.5.1 Eutrophication Control

Remarkable increases in urbanization during the past century in China have resulted in major changes in the ecology of Chinese inland waters (Dudgeon et al. 1993). Increased anthropogenic inputs from household, agricultural, and industrial effluents have turned many inland waters eutrophic and urban lakes hypoeutrophic. These changes are most notable in the lakes close to large population centers (Shu 1991). To mitigate the increased nutrient loads, various approaches have been used: (1) to reduce, remove, or divert the nutrient loadings from the sources to lakes; (2) to channel the increased nutrients for the production of aquatic products such as food and fish, which are then harvested, thus removing the nutrients; and (3) to dredge the lakes to remove nutrient-rich sediment.

As noted earlier, beginning in 2007, the Wuxi City Environmental Protection Bureau and the Jiangsu Provincial Government forced hundreds of small chemical and manufacturing plants near Lake Tai to close or relocate to cut down pollution and influx of N and P. The results have been improved river conditions and a leveling off of the amount of industrial wastes in the lake.

Since more than 70 % of urban eutrophication is owing to point-source inputs of industrial and household effluents, reduction and diversion of these sources of loading are needed to reduce lake enrichment (Jin et. al. 1990). Waste water treatment plants are an efficient means of retrieving a large quantity of nutrients and organic matter from point sources. Some of the large cities in China, including Shanghai, Beijing, and Hangzhou, began to construct sewage treatment plants in 1990s to reduce waste loading of inland and coastal waters.

As for large lakes, pollution predominantly enters through river systems and originates primarily from urban sources and agricultural effluents. Removal of the nutrient loads from river systems by biological nutrient uptake techniques using aquatic plants has been tried at many selected sites in the tributaries of Lakes Tai and Chao, but is still in the experimental stage. These experiments have shown that these plants are responsible for substantial uptake of nutrients and heavy metals but to date, this methodology is not very efficient in controlling eutrophication and its application is often limited by the type of plants available and by limitations on their active growing periods.

Most of the large lakes in the PDB are shallow and meromictic. Reducing loadings from external nutrient sources to shallow lakes has a limited effect on the reduction of eutrophication, because sediment resuspension plays a significant role in contributing nutrients to the water column. Sediment removal has been used to reduce the level of eutrophication in these lakes (Chang 1993).

Another approach involves channeling the increased nutrients for food and fish production, then removing the nutrients by harvesting the aquatic products. This can be a useful yet sustainable methodology and has been used in many large lakes and impoundments. Integrated lake farming is an example of this approach. However, if eutrophication is to be controlled, the ratio between stocking fish and the biomass of aquatic macrophytes must be adjusted so that the large amounts of nutrients released by remineralization by fish can be absorbed by plants (Chang 1994). So far, such systems appear to contribute to the additional nutrients through the remineralization by fish.

8.5.2 Institutional Coordination

As noted earlier, large lakes in China are governed by several different agencies of the central government in Beijing. The Ministry of Water Resources has authority over flood control and regulation of water level and as a part of this authority, it controls the timing for closing and opening the floodgates of dams. The Ministry of Agriculture has responsibility for managing fisheries, particularly fish production, and aquatic natural resources. NEPA is responsible for pollution monitoring, control, and regulation. However, since many of these mandates are not coordinated, management conflicts have arisen.

The conflict posing the greatest concern deals with the regulation of water levels in lakes by controlling the opening and closing of floodgates (Pu et al. 1989). Decisions regarding opening and closing of the floodgates are in the hands of the water resources authority. In most cases, the floodgates are raised in winter to drain lake water and are closed for most of the rest of the year. Fish recruitment, however, occurs in spring when the fish spawn in rivers and the larvae find their way to lakes to settle. Prior to the construction of dams and weirs in Chinese waterways, recruitment occurred every spring. After the constructions of these dams and weirs and the adoption of new ways of managing water levels, natural recruitment no longer took place in most inland waters. This has led to depletion of many fish species and of other

aquatic resources in lakes. A coordinated approach to lake management by the various oversight agencies is needed. The need for strong institutional coordination increases with the increased use and abuse of lake resources. Furthermore, the responsibility for managing lakes and for coordination among agencies should be given to the regional lake commissions, whenever possible, since the regional lake commissions are familiar with the local environment and can best accommodate the specific local needs for the enhanced use, protection, and operation of lakes.

8.5.3 Control of Wetlands and of Littoral Resources

The wetland and littoral zones are important areas for fish spawning, nesting ground for birds, reducing the influx of pollutants, and controlling erosion. However, the wetland and littoral zones of the large lakes in China's PDB are vanishing quickly as these areas face increasing pressure for development. Owing to the population expansion over the past two decades and to the expanded economic development, which began in the 1980s, the wetlands and littoral areas in the PDB are now disappearing at even faster rates than in the 1970s. Many wetlands are currently used not only for farming, but also for housing developments and factories. An absence of legal restraint on development and the lack of overall conservation planning for wetland and littoral zones are largely responsible for this abuse. It is, therefore, highly recommended that an integrated lake basin development program be established to control abuses and to foster the conservation of these critical zones.

The riparian and littoral zones have long served as filters for reducing sedimentation and the influx of nutrients and toxic substances into lakes. The use of littoral and riparian systems to control nutrient loadings and the influx of toxic substances can be a low-cost method of reducing eutrophication and toxic pollution of lakes. The establishment of riparian zones along lakes and waterways has been found to be effective in protecting inland waters in North America. It is highly recommended that China establishes a coherent plan to manage its riparian zones in the absence of monitoring programs and effluent controls, because the PDB has a high population density, increased nutrient loadings, and large influx of toxic substances. Such a zone can at least serve as a first line of protection by reducing the amounts of wastes entering the lakes. Lake Tai authorities are currently contemplating the creation of a buffer zone several hundred meters in width, where near-shore farms and villages would be converted into wetlands and parks, but such relocation plan close to urban centers will be costly.

8.5.4 Management Strategy

With its enormous population and increasing use of large lakes, China needs to integrate the lake management programs and to plan for sustainable use of its aquatic resources. The management plan should take into consideration the environmental costs of development and the ecological service that lakes provide, and should reduce the current focus solely on boosting aquatic production and on the use of the lake for waste disposal. The reduction or recycling of wastes needs to be encouraged by industries, which are responsible for waterborne hazards such as industrial toxins and untreated sewage, and for losses in aquatic habitats. Mounting public concern about drinkable water, clean lakes, and sustainable natural resources has begun to bring about an awareness of better integrated plans for managing inland waters. Such awareness, however, is far from the elaboration of an integrated lake development strategy, which would include plans for watershed development, control of waste run-off, sustainable resource management, and the effective protection and management of surface waters. Continued encouragement and promotion of environmental consciousness is necessary, since incentives in China for focusing on sustainable uses of inland waters are not high. Instead, people's primary concerns are near-term profits. Annual growth in GDP has been considered more important than environmental protection and conservation. This attitude is characteristic even of most water and lake management authorities. To increase awareness of more sustainable lake management alternatives, international funding organizations can play an important role in persuading local officials to include environmental costs and the protection and conservation of natural resources in development projects, and to encourage local authorities to form integrated development teams. Such teams would involve developers, environmental scientists, county/city officers, and village representatives in project planning from the onset. The ultimate responsibility for managing a large lake environment rests upon all citizens living in its watershed. Unless the majority of citizens recognize the importance of sustainable uses of lakes and are willing to protect these precious resources, many large lakes in China will cease to serve the people who have depended on them over thousands of years.

8.6 Summary

Anthropogenic inputs to China's great lakes in the PDB have been increasing since 1950, as population and human activities in their immediate watersheds have increased. However, the rate of the change was slow in the 1960s, the types of the inputs during those periods were primarily agricultural and household wastes, and the amounts involved were relatively low. During

the 1960s, large lakes were generally oligotrophic with inputs of primary organic matter from the immediate watershed.

The new economic initiatives of the 1980s stimulated major industrial development, resulting in a great increase in industrial effluents. In addition to nutrient inputs, high levels of metals and toxic organics have already been found in lake sediments and benthic fishes in China's great lakes, such as Lakes Tai and Chao. These contaminants include mercury, arsenic, phenol, copper, cyanide, zinc, lead, and chromium, and can be readily associated with the nearby major industrial sources. Large lakes in this basin became mesotrophic to eutrophic with the beginning of blue-green algae blooms.

Lakes Tai and Cao have now become hypereutrophic. Lake Cao has 192 and 3,035 μg L^{-1} of TP and TN, respectively, while Lake Tai's TP and TN are 108 and 1,771 μg L^{-1} based on the survey conducted in 2001–2003. Aquatic ecosystems in these lakes have undergone a major change in which systems dominated by macrophytes have been replaced by algal-dominated systems. Blue-green algae blooms in the great lakes in this basin are becoming annual occurrences, threatening water supplies and the sustainability of freshwater ecosystems.

These lakes have changed from oligotrophic to hypereutrophic in the last 40 years. Continuing disposal of untreated domestic and industrial wastes contributed significantly to this change. Lake management practices, such as dams and weirs for flood control and extensive use of littoral area and wetland for farming, aquaculture, and home construction, have also contributed to the acceleration of this process.

With its enormous population and increasing use of its great lakes, China needs to integrate its lake management programs and to plan for sustainable use of its aquatic resources. The management plan should take into consideration the environmental costs of development and the ecological service that these lakes provide. The reduction or recycling of wastes by industries needs to be closely controlled. Continued encouragement and promotion of environmental consciousness is necessary, and promotion of sustainable uses of inland waters and involvement of average citizens to contribute to the joint decision in environmental planning and lake management are a key to the success of managing these important water bodies.

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Photoautotrophic Productivity in Eutrophic Ecosystems

9

Martin T. Dokulil

Abstract

Enhanced photoautotrophic productivity of lakes, reservoirs, rivers and streams is a consequence of prolific nutrient loading from the catchment known as eutrophication. In most cases, it is a syndrome of ecosystem responses to human activities in the watershed. Primary production is strongly influenced by latitude, insolation and nutrient availability, but also depends on lake size, the size of the catchment, the type of water body and lake depth. The outcome is therefore highly variable for specific continental waters. Nevertheless, autotrophic production is perhaps the best parameter to define the trophic level of waters. The complex techniques and frequent measurements necessary to estimate production accurately hampered the application, however. Recent improvements in methods and new developments in monitoring strategies have revived interest in primary production as an index to define trophy. Important relationships of production to environmental variables are analysed. Then, development of boundary criteria are discussed, production indices compared and trophic boundary classifications compiled from different authors. Maximum and global production is emphasised. The impact of a warmer world as a consequence of climate change on continental waters is highlighted and future perspectives of photoautotrophic production summarised.

Keywords

Productivity · Continental waters · Eutrophication · Trophic indices · WFD

9.1 Introduction

Eutrophication is the process of increased productivity of lakes, rivers and estuaries as a consequence of increased nutrient input from the water shed. The process of eutrophication can be natural but is in most cases a syndrome of ecosystem responses to human activities in the catchment. Accordingly, production of plants, bacteria and animals usually increase but the outcome is highly variable. Phytoplankton primary production is strongly influenced by latitude (Brylinsky and Mann 1973; Boulion 2003), insolation (e.g. Jónasson 1974; Anderson 1974) and nutrient availability (e.g. Schindler 1978), but also depends on lake size, the size of the catchment, the type of water body and lake depth (Fee 1979, 1980; Knoll et al. 2003; Nõges 2009).

Primary production is a fundamental ecological variable. It is a measure of the extent to which primary energy input by solar energy to the aquatic environment is transformed and accumulated into biological entities adding organic substance to the ecological sphere. Because production is defined as the flux of inorganic carbon into autotrophic organisms per unit time, this rate can be used as an indicator of growth and hence as a major criterion to determine the

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trophic state of a water body. Trophic categorization based on phytoplankton productivity, however, is based on the assumption that inputs from littoral or allochthonous sources are negligible. On a global basis, productivity from the littoral or of external origin can be much larger than phytoplankton production in many cases (Wetzel 1990).

The original concept of the trophic system aims to arrange surface waters, regardless of their size and ecological characteristics, in a continuous sequence of increasing trophy. The basis for comparison is the intensity of organic production (Ohle 1958). The autotrophic capacity of a lake or a river therefore appears to be an ideal basis for establishing an absolute scale of trophic level (Elster 1954, 1958; Winberg 1960). Hence, 'trophy' is often directly equated with the intensity of primary production, which should better be termed 'autotrophic production' following argumentation by Flynn (1988).

The aim of this chapter is to gather and critically evaluate information on the use of primary production criteria to define trophic boundary conditions, particularly for variable eutrophic systems.

9.2 Lakes, Data and Methods

The lakes covered in this study range from ultra-oligotrophic Arctic lakes to hypertrophic tropical lakes, include shallow and deep lakes, high mountains and flatland lakes from around the world. If not otherwise stated, the data used in this compilation are original or come from information summarised in Dokulil (2005) for alpine lakes, Dokulil et al. (2005) for a variety of lake types, Håkanson and Boulion (2001) for lakes from the former Soviet Union (their Annex A) and Kimmel et al. (1990) for reservoirs.

Carbon uptake can conveniently be estimates using the ^{14}C-technique developed by Steemann Nielsen (1951) or one of its modifications (Dokulil and Kaiblinger 2009). Incubation periods of equal or less than 2 h are considered to represent gross uptake. Alternatively, photosynthetic oxygen evolution or fluorescence signals can be measured (Dokulil et al. 2005; Dokulil and Kaiblinger 2009). For details on methods and conversions to carbon, refer to Wetzel and Likens (1991, p. 207 ff.) and Kaiblinger and Dokulil (2006).

Chlorophyll-a (chl-a) is used here as a universal indicator of algal biomass and was measured by extraction in either acetone or ethanol followed by photometrical determination (Lorenzen 1967, ISO 10260 1992).

Production estimations reported as oxygen rates were converted to carbon using a factor of 0.3 mg C per mg O_2 assuming an assimilation coefficient of 1.25. Hourly rates of photosynthesis were converted to daily rates using appropriate day length conversion (day light hours × 0.6; Talling 1957).

9.3 Primary Productivity Relationships

Almost all definitions of trophic categories are primarily related to nutrient concentration and loading from the catchment (Rast and Thornton 2005). Klapper (1992) related average annual integrated primary production (ΣΣP) to total phosphorus (TP) concentration at spring overturn (Fig. 9.1).

A similar relation to soluble reactive phosphorus at spring overturn (SRP_{SP}) was reported by Fricker (1981). Daily and annual production was correlated with TP, SRP_{SP} and to TP concentrations predicted from models (Clasen and Bernhardt 1980; Fricker 1980; Vollenweider and Kerekes 1980; OECD 1982). Håkanson and Boulion (2001) have related TP to maximum and mean volumetric daily production in their extensive study, trophic relations. Similarly, production estimates from clear and humic lakes were correlated to chl-a and TP by Nürnberg and Shaw (1999). A recent meta-analysis examined the effects of several variables including nutrients on absolute and relative production estimates (Faithfull et al. 2011). One of their conclusions was that both P and N can be predictors of primary production. This well-established, positive relationship between loading and productivity becomes apparent when phytoplankton biomass increases as a consequence of eutrophication (e.g. Harper 1992). Eutrophic and hypereutrophic lakes can sustain very high algal biomass often dominated by few taxa. In such systems, however, total phytoplankton biomass as well as all groups except blue-greens and diatoms tend to flatten off (Watson et al. 1992, 1997). This curvilinearity is also evident during the oligotrophication process (Jeppesen et al. 2005). Phytoplankton biomass can be estimated indirectly using chl-a as a surrogate parameter. Both variables correlate well as has been demonstrated many times (e.g. Huot et al. 2007). The chl-a therefore remains the best proxy of phytoplankton biomass for studies of primary productivity (Huot et al. 2007).

The chl-a correlates with daily photoautotrophic production (A) over a wide range of trophic levels from ultra-oligotrophic arctic lakes to highly productive tropical lakes in Africa (Fig. 9.2).

Average volumetric production in the euphotic zone directly depends on mean chl-a concentration. The correlation of the 214 observations is highly significant ($r^2 = 0.81$, $p < 0.001$). The 95% confidence limits remain narrow over the entire range (4 orders of magnitude) indicating good agreement between variables. This close relation allows designation of empirical trophic boundaries (Fig. 9.2). These boundaries omit average values as suggested by the regression equation and is orientated towards accommodation of all production rates in each trophic category.

To model photoautotrophic production from chl-a (Håkanson and Peters 1995; Bot and Colijn 1996; Morin et al. 1999), additional information on the relationship with incoming radiation is required. Daily column production

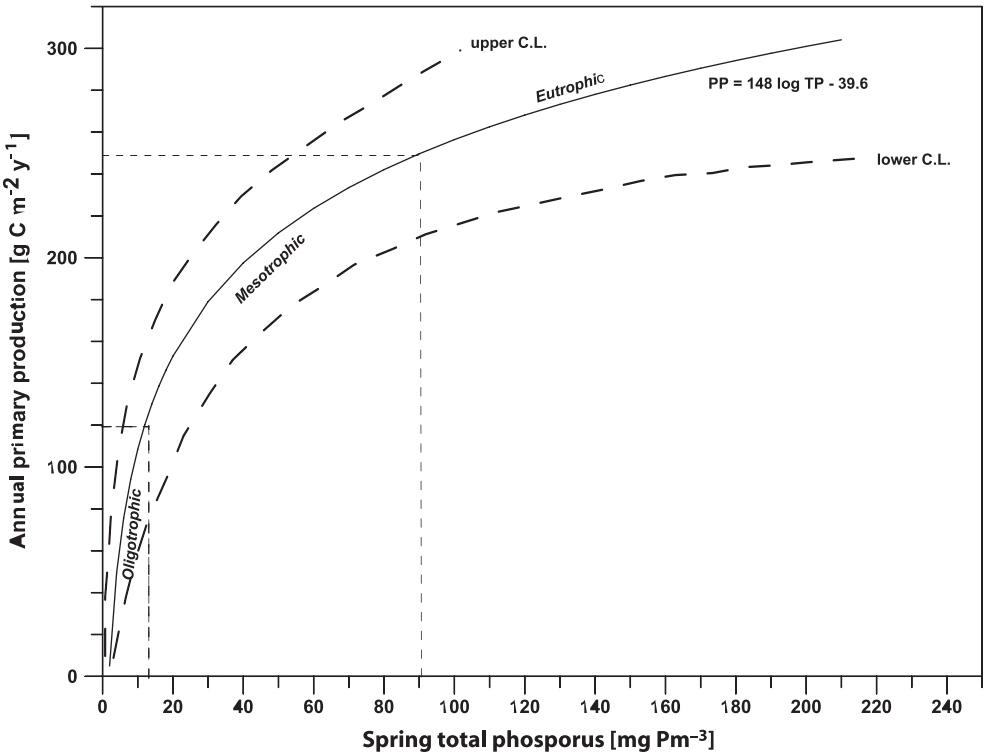

Fig. 9.1 Fitting annual primary production to spring total phosphorus concentration. The equation, 95 % confidence limits (C.L.) and approximate trophic delineation are given in the diagram. (Modified from Klapper 1992)

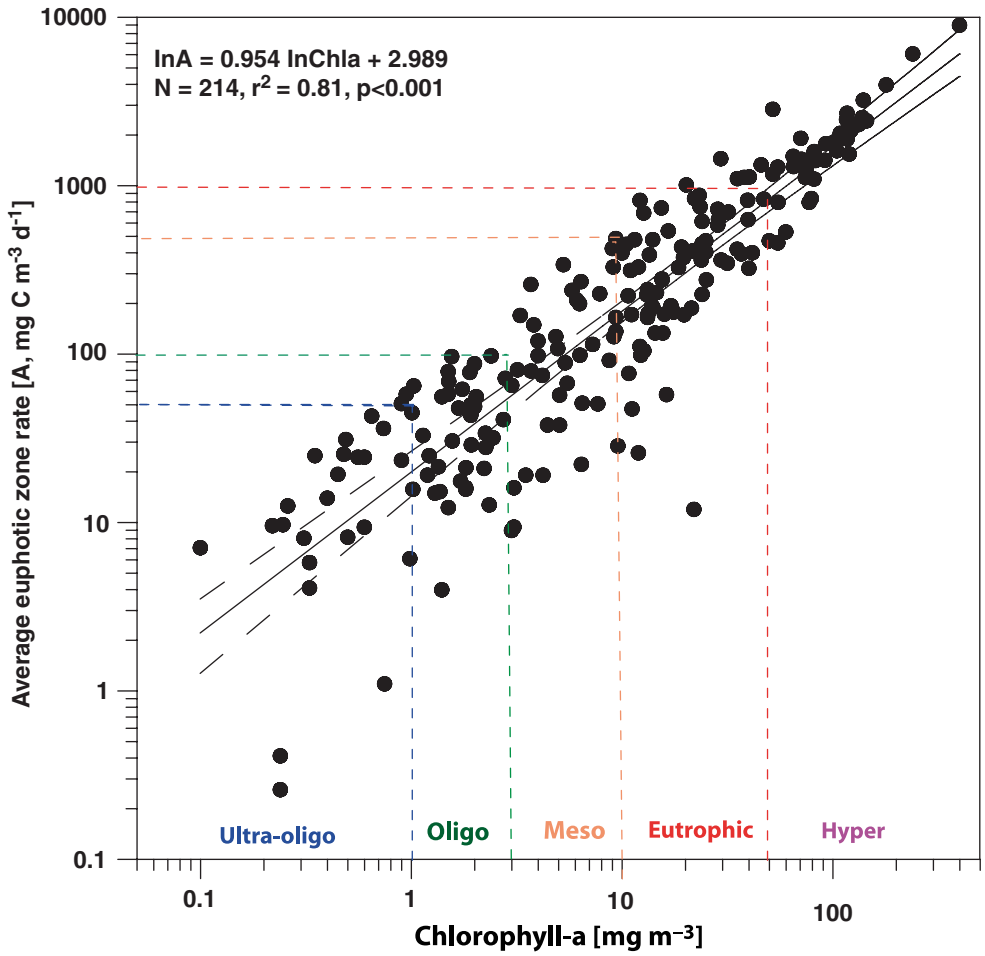

Fig. 9.2 Dependence of average daily euphotic zone production rate (A) on chl-a using data from Kimmel et al. 1990; Håkanson and Boulion 2001; Dokulil 2005 and Dokulil et al. 2005. Log-log plot. The equation, statistical data and 95 % C.L. and trophic boundaries are inserted in the diagram

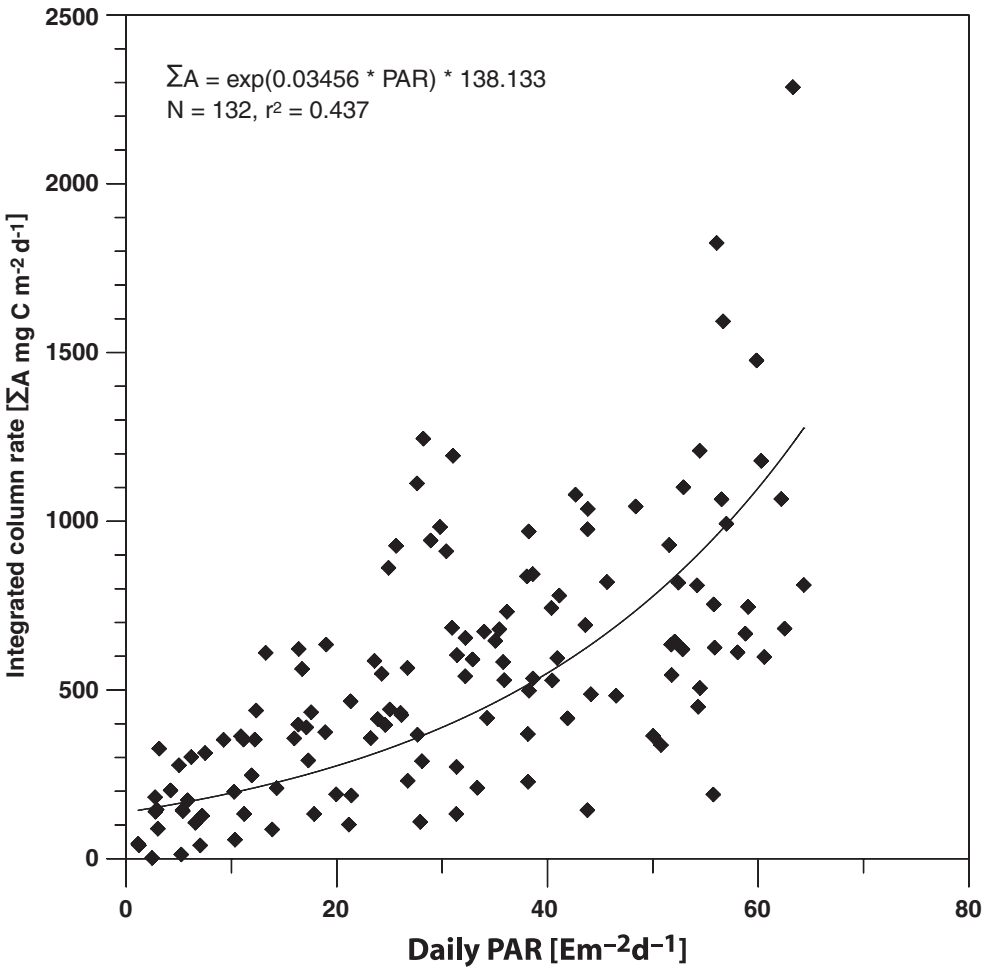

Fig. 9.3 Daily integrated column production related to daily insolation as hotosynthetic active radiation (PAR) using data from Kabas 2004

(ΣA) correlated with daily photosynthetic available radiation (PAR) in an urban lake in Vienna, Austria (Fig. 9.2). Jónasson et al. (1974) reported significant correlation of annual average production to solar radiation (Fig. 9.3).

In a turbid lake, ΣA was more loosely related to PAR because of highly variable underwater light attenuation (Lind et al. 1992). As a further consequence of this light relationship, production estimates were significantly linked with latitude (Brylinsky and Mann 1973; Nürnberg and Shaw 1999; Håkanson and Boulion 2001; Faithfull et al. 2011). Although regulation of ΣA by latitude alone is unlikely, as much as 50–74% of the variability of ΣA is explained by latitude. The ΣArate has also been shown to be highly dependent on watershed land use in a reservoir study by Knoll et al. (2003) while production at the best depth (A_{opt}) correlated significantly with chl-a and TP. From these data, the authors conclude that land use sets an upper limit to primary production.

9.4 Developing Trophic Boundary Criteria

Vollenweider (1968) considered it difficult to suggest a simple unequivocal correlation between production capacity and trophic level. One of his basic concerns was the correct choice of reference values and their space and time dimensions used for comparison. A logic option is the annual carbon uptake per unit surface area (ΣΣP), which allows comparison of lakes and also to relate them to other ecological units such as estimates of terrestrial or marine primary production (Geider et al. 2001). Complications, however, arise from the large variability of lake size and depth affecting not only the amount of production rates but also the shape of the depth profile. Variable underwater light attenuation owing to external factors or feedback mechanisms as a consequence of increasing algal abundance during eutrophication additionally influences column production per square metre. Moreover, complex and time-consuming methodology further hampered the application of photosynthetic rate measurements to define trophic situations. As a consequence of these difficulties, other variables became more popular as indicators to define boundaries of trophic categories (see e.g. OECD 1982).

Recent improvements in measuring techniques and new developments in monitoring strategies have revived interest in primary production as an index to define trophy (Andersen et al. 2006) although there is still a controversy about the measurement units (Smith 2007). One alternative unit already discussed by Vollenweider (1968) is the ‘activity

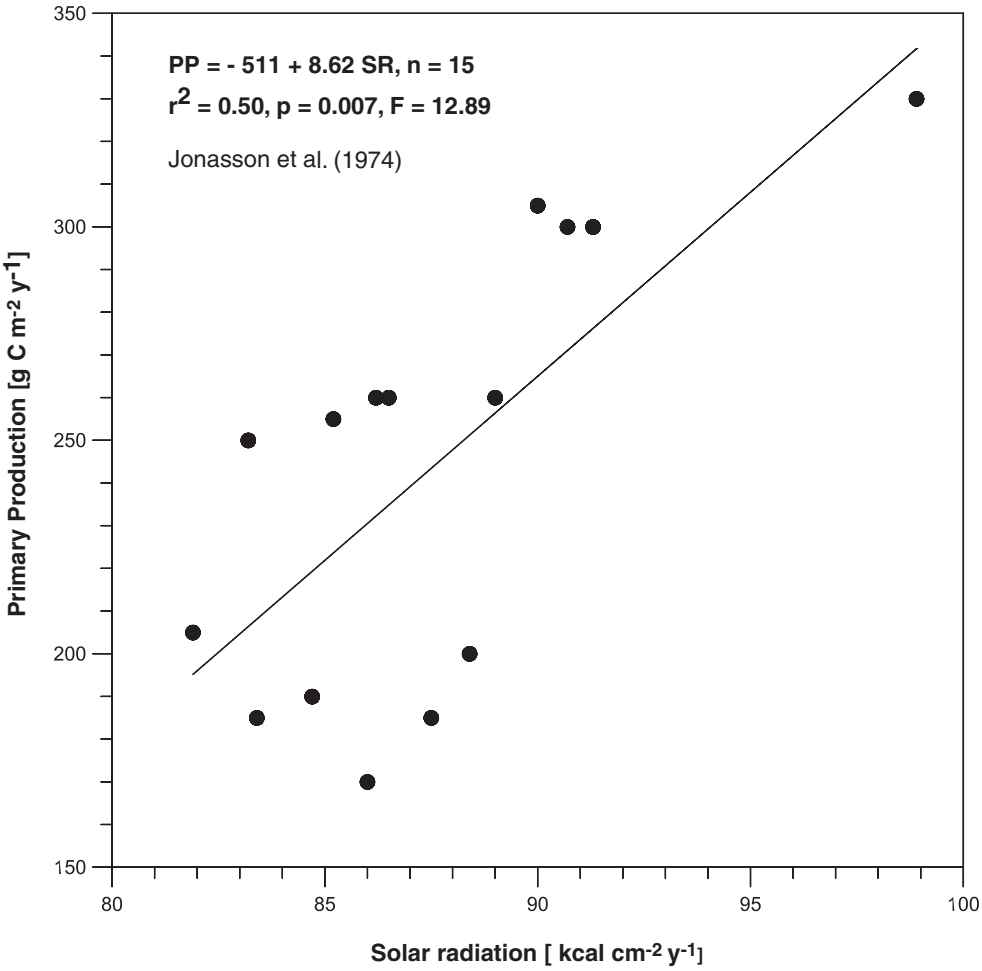

Fig. 9.4 Regression of annual primary production on solar radiation modified from Jónasson et al. (1974). Statistical analysis is inserted into the graph

coefficient' defined as carbon uptake rate per algal unit measured as cell, biomass, chl-a and carbon content. Such coefficients are sensitive indicators to describe the physiological state of algal assemblages but are not suitable for the demarcation of trophic levels because their quantities usually all fall into a narrow range of values (see e.g. Dokulil et al. 2005; Fig. 9.4).

The controversy about the correct reference to define trophic boundary conditions from photosynthetic rate measurements substantiated in different entities used. According to Findenegg (1964), the vertical distribution of daily production often is a better indicator of trophy than integrated rates (Dokulil et al. 2005; Dokulil and Kaiblinger 2009). Using the data on average volumetric euphotic zone production (A) from Fig. 9.2 and the delineation proposed therein, a gradient of trophic categories can be produce from the 252 observations (Fig. 9.5).

The number of data points at each trophic level indicates a slight under-representation of hypereutrophic examples. If the two oligotrophic levels are considered as one category as well as the two eutrophic levels, their number of data points, 95 and 93 respectively, are almost the same, which indicates that both trophic groupings are equally represented in the data set. Confidence intervals (notches, Fig. 9.5) show that results are statistically significant because they do not overlap. The inter-quartile range (IQR) systematically increases from 16.7 at the ultra-oligotrophic level to 1,529 at the hypertrophic end demonstrating the high variability of production rates under eutrophic conditions. The minimum–maximum range of ultra-oligotrophic waters spans 3 orders while all others vary between 1 and 2 orders.

A volumetric production at optimum depth (A_{opt}) of about 200–300 mg C m^{-3} d^{-1} has been suggested by Vollenweider (1968) as a boundary setting between oligo-mesotrophic and Eu-hypertrophic waters. Integral column production (ΣP) can be estimated from A_{opt} using modifications of a simple model developed by Talling (1957, 1970), which proved useful in many cases but underestimates under-hypertrophic conditions (Robarts 1984). For a nutrient-rich turbid tropical lake, empirical estimates were possible from a combination of A_{opt}, chl-a and euphotic depth z_{eu}

$$\Sigma P = 2.5(A_{opt} \cdot \text{Chl-a} \cdot z_{eu}) + 46.8 \qquad (9.1)$$

Column production (ΣP) increasingly depends on the most productive layer (A_{opt}) the higher the trophic level is of a lake (Rodhe 1958). This observation was used to define trophic levels from the relation daily carbon uptake rate at

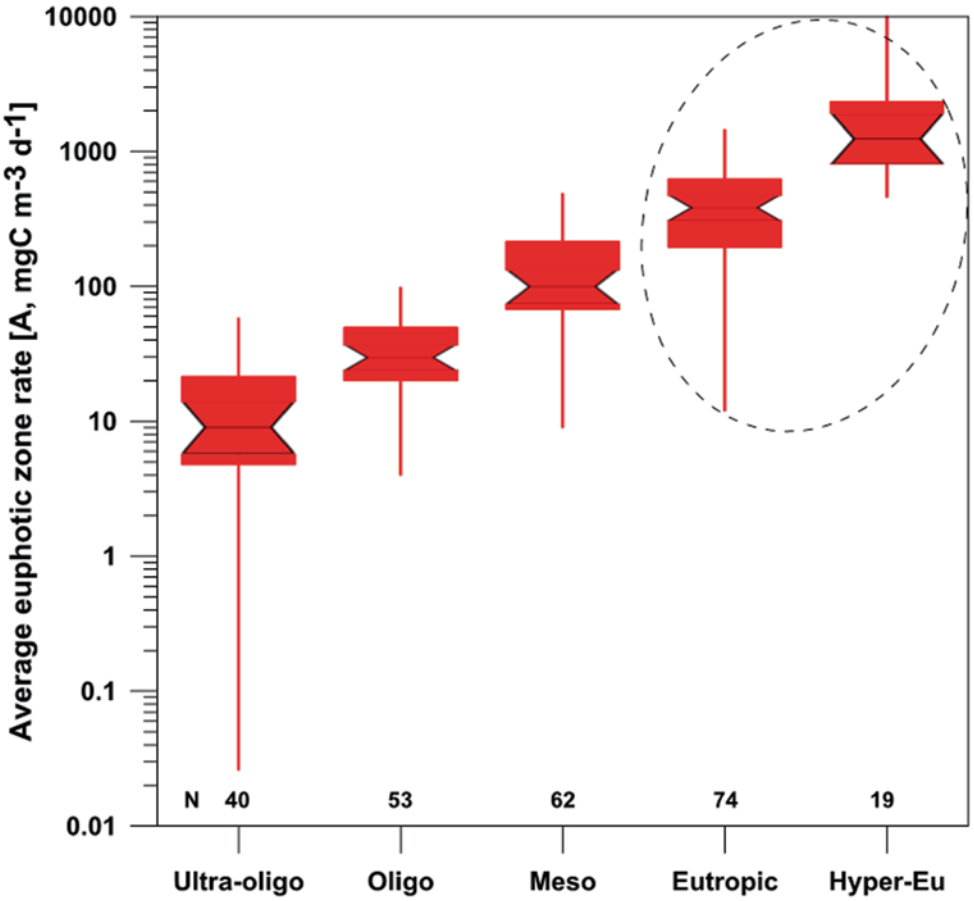

Fig. 9.5 Notched box whisker graphs of the average euphotic zone rates

optimum depth to daily column carbon production (Klapper 1992, p. 79)

$$\frac{A_{opt}}{\Sigma P}\ \frac{mgCm^{-3}d^{-1}}{mgCm^{-2}d^{-1}}(\%) \tag{9.2}$$

Oligotrophic	Mesotrophic	Eutrophic	Polytrophic	Hypertrophic
≤15	15–30	30–75	75–90	>90

A graphical approach modified from Vollenweider (1968) provides an elegant summary of the volumetric versus integrated rate controversy (Fig. 9.6).

A range of maximum and mean attenuation coefficients supply additional information on light availability, water transparency and indirectly on lake depth. As optimum carbon uptake rates at varying attenuation coefficients increase, column production tends to decline because of reduced light availability (higher attenuation coefficients) as a consequence of self-shading by enhanced algal biomass. Figure 9.6 also illustrates the potential variability of carbon uptake rates within a broad range of possible attenuation coefficients representing clear to turbid conditions. The potential range, however, is strongly reduced at high trophic level. Some examples of individual lakes or geographical regions are inserted to demonstrate the range of carbon uptakes commonly encountered. Some examples from European alpine lakes can be found in Dokulil (2005; Fig. 9.6). Eutrophic lakes in warm regions of the world such as Egypt, East Africa and China are good examples of highly productive waters. The theoretical maximum rate, which has been derived from theoretical considerations by Vollenweider (1965a), can be described by an exponential equation

$$\Sigma P = 2952.563 \times (1 - \exp(-0.014A_{opt})) + 2595.813 \times (1-\exp(-0.00094A_{opt})),\ r^2 = 0.99,\ p < 0.0001 \tag{9.3}$$

Based on earlier arguments and formulations, Bannister (1974) developed an equation for the upper limit of production, which is identical to the one given by Vollenweider (1968, p. 43).

$$\Sigma P\ [g\ Cm^{-2}\ d^{-1}] = f_i \times A_{opt}/k_w \tag{9.4}$$

with f_i=2.5 (2 – 3.5)—Vollenweider (1968), f_i=2.3—Bannister (1974) and k_w attenuation coefficient.

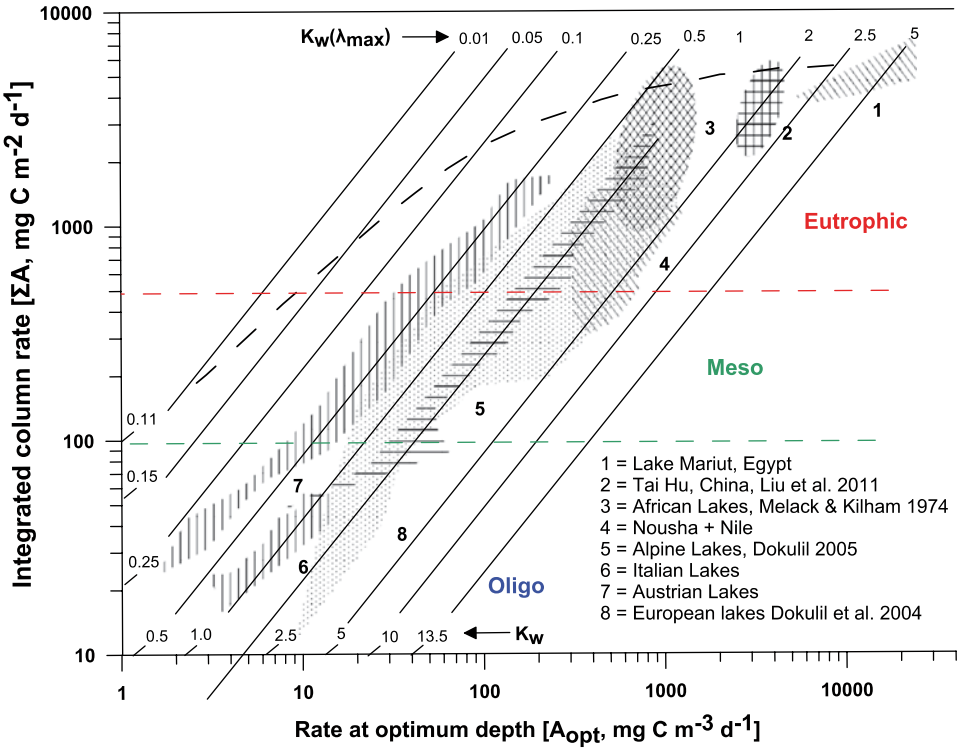

Fig. 9.6 Daily integrated column rate (ΣA) versus rate at optimum depth (A_{opt}) for different minimum attenuation coefficients (*diagonal lines*, $K_w(\lambda max)$ and total attenuation K_w) The *dashed line* indicates theoretical upper limits of production (see text for further explanation). Different shadings show the area of different lake regions or specific lakes in the world. Numbers in the legend specify these lakes and are, if not otherwise stated, from Vollenweider (1968). Trophic limits inserted. Diagram modified from Vollenweider (1968)

Similarly, annual production (ΣΣP) can be predicted from chl-a concentration, light attenuation coefficient (k_w) and the chl-a specific extinction coefficient (η) using an equation developed by Vollenweider (Clasen and Bernhardt 1980)

$$\Sigma\Sigma P\,[\text{g C m}^{-2}\ \text{y}^{-1}] = K\frac{Chl-a}{k_w + \eta \times Chl-a} \qquad (9.5)$$

A more intensive discussion of depth-time integrated production calculation and associated models can be found in Rodhe (1965) and Vollenweider (1965a, b, 1970).

Kimmel et al. (1990) provided a detailed table of the magnitude and variability of ΣA in reservoirs of different trophy. On an annual basis, phytoplankton production is not significantly different from phytoplankton production in natural lakes (Brylinsky 1980; Wetzel 2001, p. 386 ff.). Daily productivity in most reservoirs, however, is likely more variable than in most natural lakes. About 30–40 % of the lakes and reservoirs included in these references are eutrophic. This is certainly an underestimation because most of the waters worldwide are small and shallow with plenty of light and nutrients (Downing et al. 2006; Downing 2010). This group therefore should be among the most productive systems of the world (Lewis 2011). Similarly, productivity of large rivers is likely to rise owing to increasing eutrophication (Dokulil 2012). Global change will further enhance freshwater eutrophication (Dokulil and Teubner 2011).

9.5 Defining Trophic Boundary Conditions

Trophic boundaries were commonly deduced from column integrated rates per square metre of lake surface (mg m^{-2}) either per day or per year.

Boundaries defined for integral daily rates by Henderson-Sellers and Markland (1987) in Table 9.1 are not very different from those by Schönborn (2003). Trophic levels were expanded to cover hypertrophic conditions by Håkanson and Boulion (2001).

Their ranges of average annual production (Table 9.2) are much lower for the trophic categories than those stated by Schönborn 2003 (Table 9.1).

Håkanson and Boulion (2001) then further added an ultra-oligotrophic level basing trophic classification on fixed steps of mean summer chl-a using a factor of 10 (Table 9.3) which was also used earlier by Håkanson and Peters (1995; Table 9.3) in their modelling approach.

Limits by Wetzel (2001) are higher particularly for eutrophic conditions. In addition, his system expands the trophic categories by adding ultra-oligotrophic and dystrophic levels (Table 9.4)

Klapper (1992) and Felföldy (1987) considerably expanded and refined trophic categories to be able to better differentiate lakes in regions where waters are primarily at higher trophic level (Tables 9.4 and 9.5).

Table 9.1 Ranges of chlorophyll-a (chl-a), daily column production and annual production for three trophic levels

Trophic level	Chl-a[a] (mg m^{-3})	Daily production[a] (mg C m^{-2} d^{-1})	Daily production[b] (mg C m^{-2} d^{-1})	Annual production[b] (g C m^{-2} y^{-1})
Oligotrophic	0–4	30–100	0–200	<100
Mesotrophic	4–10	100–300	200–500	100–150
Eutrophic	*10–100*	*300–3,000*	*500–4,000*	*150–250*

[a]Modified from Henderson-Sellers and Markland (1987, p. 200)
[b]Modified from Schönborn (2003, p. 255)

Table 9.2 Trophic boundaries of total phosphorus (TP), chlorophyll-a (chl-a), algal fresh weight and yearly production for four trophic levels. (Modified from Håkanson and Jansson 1983)

Trophic level	Total-P (mg m^{-3})	Chl-a (mg m^{-3})	Algal fresh wt. (g m^{-3})	Annual production (g C m^{-2} y^{-1})
Oligotrophic	<10	<2.5	<0.8	<30
Mesotrophic	8–25	2–8	0.5–1.9	25–60
Eutrophic	*20–100*	*6–35*	*1.2–2.5*	*40–200*
Hypertrophic	*>80*	*30–400*	*2.1–20*	*130–600*

Table 9.3 Trophic classification based on fixed steps (factor 10) of mean summer chlorophyll-a (chl-a) concentrations and adding an ultra-oligotrophic level. (Modified from Håkanson and Boulion 2001)

Trophic level	Total-P (mg m^{-3})	Chl-a (mg m^{-3})	Daily rate (mg C m^{-3} d^{-1})	Annual production (g C m^{-2} y^{-1})
Ultra-oligotrophic	<3	≤0.1	≤4.4	≤12.5
Oligotrophic	1–10	≤1	≤32	12.5–38
Mesotrophic	5–40	≤10	≤270	38–140
Eutrophic	*20–400*	*≤100*	*≤2,400*	*140–640*
Hypertrophic	*>100*	*≤1,000*	*>2,400*	*>640*

Table 9.4 Trophic classification for seven trophic categories based on chlorophyll-a (chl-a) and column production either per day or per year

Trophic level	Chl-a[a] (mg m^{-3})	PP[a] (mg C m^{-2} d^{-1})	Chl-a[b] (mg m^{-3})	PP[b] (g C m^{-2} y^{-1})
Ultra-oligotrophic	0.01–0.5	<50		
Oligotrophic	0.3–3	50–300	<3	<120
Mesotrophic	2–15	250–1,000	3–10	120–250
Eutrophic	*10–500*	*>1,000*	*10–20*	*250–400*
Polytrophic			*20–60*	*400–500*
Hypertrophic			*>60*	*>500*
Dystrophic	0.1–19	50–500		

[a]Modified from Wetzel (2001, p. 389)
[b]Modified from Klapper (1992, p. 79)

Table 9.5 Trophic boundaries for chl-a, daily column production and annual production dividing the trophic continuum into nine trophic levels. (Modified from Dokulil 2003 after Felföldy 1987)

	Chlorophyll-a (mg m^{-3})	Daily production (mg C m^{-2} d^{-1})	Annual production (g C m^{-2} y^{-1})
Ultra-oligotrophic	<1	<50	<10
Oligotrophic	1–3	50–125	10–25
Oligo-mesotrophic	3–10	125–250	25–50
Mesotrophic	10–20	250–500	50–100
Meso-eutrophic	20–50	500–900	100–175
Eutrophic	*50–100*	*900–1,500*	*175–300*
Eu-polytrophic	*100–200*	*1,500–2,500*	*300–500*
Polytrophic	*200–800*	*2,500–4,000*	*500–800*
Hypertrophic	*>800*	*>4,000*	*>800*

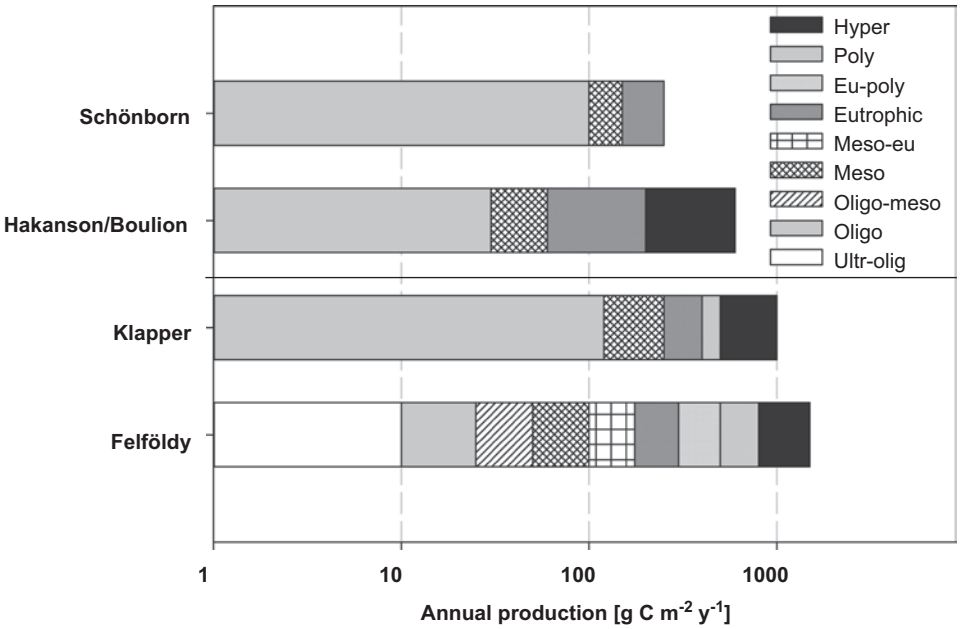

Fig. 9.7 Comparative graphical representation of trophic boundary conditions from four authors using data for annual average column production from Tables 9.1, 9.2, 9.3 and 9.4. Note logarithmic x-axis

Both systems have similar boundaries at both average daily and annual rates. The annual boundaries proposed by these authors are compared in Fig. 9.7.

9.6 Global Production

In a recent analysis on global primary production of lakes, Lewis (2011) concluded that maximum rates of photosynthesis centre at about 10 g C m^{-2} d^{-1}, equivalent to 3,650 g C m^{-2} y^{-1}. Earlier estimates range from 8–13 g C m^{-2} d^{-1} (Melack and Kilham 1974; Uhlmann 1978; Talling 1982; Talling and Lemoalle 1998).

According to Pace and Prairie (2005), global gross primary production (GPP) of lakes is about 0.65 Pg C y^{-1}, which might be an underestimate since it does not emphasize the high production of small lakes, which are estimated to dominate globally (Downing et al. 2006). Within the global GPP of 100–150 Pg C y^{-1} (Randerson et al. 2002) global internal primary production of lakes represents only a minor fraction of global primary production.

Understanding global limnology and global photoautotrophic production of lakes, ponds, rivers, streams and wetlands becomes increasingly important in a warmer world (Dokulil 2009; Dokulil and Teubner 2011). We need to quantify and understand the role of continental waters within the biosphere as water becomes a limited resource. The population of the world needs aquatic services and intact inland aquatic systems for sustainable life.

9.7 Conclusions

Climatic changes anticipated for the near future will certainly strongly affect inland waters globally both qualitatively and quantitatively (e.g. Burroughs 2001). One of the most severe impacts is eutrophication impairing water quality (Ansari et al. 2011; Dokulil and Teubner 2011). Changes in trophic level will also affect classification of lakes within the Water Framework Directive (Frisk and George 2010). Trophic boundaries and reference conditions need to be adapted to accommodate these pressures. Multidisciplinary approaches are needed to maintain water supply and solve socioeconomic consequences (Bateman and Georgiou 2010; Janus 2010). Management of water resources must include long-term monitoring strategies and model development. In this context, interest in primary production measurements as the best index of trophy must be reconsidered particularly since new fluorescence techniques allow continuous recording of relevant parameters.

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Seasonal and Spatial Nutrient Dynamics in Saronikos Gulf: The Impact of Sewage Effluents from Athens Sewage Treatment Plant

10

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Abstract

This chapter provides a long-term case study illustrating responses of a coastal Gulf in the Mediterranean Sea to reduced loading of sewage. Saronikos Gulf receives effluents from the Athens metropolitan area (population over 5 million). Until 1994, sewage discharged untreated into the surface waters of Keratsini and Elefis Bays. Sewage treatment first started in the Psitallia sewage treatment plant where the wastes discharged into inner Saronikos Gulf at 63 m depth. By the end of 2004, the secondary stage of the Psittalia sewage plant was operational.

We examined nitrogen (N) and phosphorus (P) dynamics in the inner Saronikos Gulf over the last 25 years in relation to these changes in sewage input. Additionally we described changes in the environmental status of inner Saronikos Gulf. Inorganic nutrient data from 170 cruises obtained during the year 1987–2010 allow us to describe the nutrient dynamics results and data evaluation. The study was focus on changes in nutrient concentrations between three main periods:

1. Before treatment of sewage
2. During primary treatment of sewage
3. During secondary treatment of sewage

Significant changes in nutrient dynamics noticed after the operation of primary sewage treatment plant. Nutrient concentration was high in the inner Saronikos Gulf due to the high amount of primarily treated effluents. After the year 2005, when the secondary sewage treatment was operational, there was a general decrease in nutrient concentrations in the inner Saronikos Gulf.

Keywords

Saronikos Gulf · Sewage · Nutrient dynamics · Ratios · Ecological status · Eutrophication scale

10.1 Introduction

The study area covers the Inner Saronikos Gulf surrounded by the islands Aegina and Salamina and the eastern coast of Attika. The Saronikos Gulf communicates with the Aegean Sea at its south end and is bounded by the coast of Peloponnisos to the west and the coast of Attica to the north and east. Direct wastewater discharges are one of the main causes of

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increased eutrophication in many near-shore waters. Wastewater discharged into the sea through long underwater outfalls results in sewage decomposition and mineralization. Local seawater dynamics and data on meteorological conditions are of primary importance in designing a configuration of the submarine outfall (Goldman 1976; Faganeli 1981).

The Mediterranean Sea has always been considered as one of the most oligotrophic areas in the world with extremely low nutrient concentrations, especially in the eastern region (Berman et al. 1984, 1985; Dowidar 1984; Salihoglu et al. 1990; Krom et al. 1991, 1992, 1993; Yacobi et al. 1995; Herut et al. 2000; Pavlidou and Souvermezoglou 2006). The inputs of nutrients to the Mediterranean Sea are significantly lower than the outflow through the Gibraltar Strait. The nutrient concentration in the Aegean Sea of Greece is 12 times lower than the Atlantic Ocean. Data on nutrient concentration in the eastern Mediterranean Sea during the past decade showed a depletion of nutrients of the same order of magnitude as observed by McGill (1965). The nutrient concentration was in the order of Levantine > Ionian > Aegean (Pavlidou and Souvermezoglou 2006; Stergiou et al. 1997; Souvermezoglou 1989). Despite the oligotrophic character of the open Mediterranean Sea, elevated nutrient concentration indicates problem of coastal eutrophication (e.g., Eastern Coasts of Spain, Gulf of Lions, Northern Adriatic Sea, Apulian Coasts, Saronikos Gulf, Thessaloniki Bay, and Northern Coasts of Greece; Pavlidou and Souvermezoglou 2006).

Coastal areas undergo intense and continuous environmental pressure derived from a number of driving forces such as urbanization, industrialization, changes in land use, tourism development, and climate change (Airoldiand and Beck 2007). In general, the loads of nutrients increased with increasing human activity in catchments of aquatic ecosystems creating pressure on the aquatic environment. Within only a few decades, numerous oligotrophic estuarine and coastal waters have undergone a transformation to more mesotrophic and eutrophic conditions that result in an increase in phytoplankton and macroalgal biomass, increased incidences of toxic and noxious algal blooms, consequent hypoxia and anoxia, and fish and benthos kills. The variation of nutrient loadings cause a change in nitrogen to phosphorus (N:P) ratios, which control the phytoplankton composition. This plays an important role in the biochemical dynamics and the functioning of marine ecosystems.

In Greece, one-third of the population lives on the coast. Anthropogenic activities that influence the natural environment of the coastal zone in Greece are urbanization, industry, agriculture, aquaculture, tourism, recreational areas, and waste disposal. More than 80% of the industrial activities in Greece are located on the coast and pollute the coastal marine ecosystems by direct discharges of industrial and domestic wastes. Besides that, 90% of tourism activities are also located on the coast similarly affecting the marine environment with sewage effluent. Athens and Thessaloniki, the two biggest cities of Greece, are located on the coast and their sewage influences Saronikos and Thermaikos Gulfs, respectively (Anagnostou et al. 2005). Overall, the loads of N and P transferred into the Aegean Sea from the coasts of Greece were found in the range of 5,000–15,000 t P/y and 3,000–130,000 t N/y (Dassenakis et al. 2000).

Urban sewage usually treated in municipal plants to remove fats, solids, and floating materials (primary treatment); to degrade the biological content of the sewage(secondary treatment) and finally to raise the effluent quality before being discharged into the receiving water bodies (tertiary treatment) (Azzurro et al. 2010). However, according to a report, only 77% of Mediterranean coastal cities are provided with sewage treatment plants, and rest of the 23% discharge untreated wastewaters directly into the marine environment (UNEP/MAP 2004). The sewage discharge is a major problem for management of near-shore ecosystems, especially in regions like the Mediterranean Sea, which in recent decades experienced a growing urbanization of coastal areas (Azzurro et al. 2010). The coastal areas of Greece receiving nutrient loads from sewage have average soluble reactive phosphorus (SRP) concentrations in the range of 0.50 and 0.70 μM, nitrate ~1.00 μM and ammonium between 1.10 and 2.00 μM (Pavlidou 2010).

Saronikos Gulfreceives effluents from the Athens metropolitan area having population over 5 million. Until 1994, the domestic and industrial sewage of Athens discharged untreated into the surface water layer of Keratsini and Elefis Bays and only after 1994; the sewage primarily treated in the Psitallia sewage treatment plant and discharged into the inner Saronikos Gulf (see Fig. 10.1). Additionally, the secondary stage of the Psittalia sewage plant became operational by the end of 2004 affecting the ecological status of the Inner Saronikos Gulf (Pavlidou et al. 2008).

In this chapter, we provide an overview of N and P dynamics in the inner Saronikos Gulf which has undergone changes over the last 25 years because of regular sewage discharges in it from the sewage treatment plant of Athens in Psittalia Island. Additionally, the environmental status of the inner Saronikos Gulf is also examined in the coastal zones of Greek.

10.2 Description of the Area and Background Data

The study area covers the Inner Saronikos Gulf surrounded by the islands Aegina and Salamina and the eastern coast of Attika (Longitude: between 23° 08′ 45.22″ E and 23° 42′ 15.67″ E; Latitude: between 37° 38′ 28.82″ N and 38° 04′ 39.51″ N). The Saronikos Gulf communicates with

Fig. 10.1 Athens Sewage Treatment Plant in Psittalia Island

the Aegean Sea at its south end and is bounded by the coast of Peloponnisos to the west and the coast of Attica to the north and east. The islands of Salamina and Aigina and the plateau (< 100 m) between them divide the Gulf into two basins.

The western basin includes an elongated north–south through with maximum depths of ~220 m in the north and ~450 m in the south. The northern part of the eastern basin, called Inner Saronikos Gulf, is the area upon which we focus and apply our nutrient data, since it receives the treated wastes of ~5 million people from a point source that discharges into the sea bottom at 63 m water depth just south of Psittalia Island (Figs. 10.1 and 10.2). Psittalia Island is a small island (0.375 km^2) in the inner Saronikos Gulf, located between Pireus and Salamina. The Psittalia sewage treatment plant, located on Psittalia Island, is the second largest treatment plant in Europe. Until 1994, the sewage of the Athens City discharged untreated into the surface waters of Saronikos Gulf. During the period 1994–2004 the sewage has been primarily treated in the Psittalia Island treatment plant and diverted to the sea surface using multiport diffusers at the depth of 63 m.

A significant decrease of 35% in the organic load discharging in the marine environment was achieved. The biochemical oxygen demand (BOD) of the treated sewage was between 160 and 250 mg/L. By the end of year 2004 secondary treatment of sewage started in Athens. Approximately 800,000 m^3 d^{-1} of treated waste discharged into the inner Saronikos Gulf, carrying $\sim 100 \times 10^6$ gC d^{-1}. This area is practically flat with a mean depth of ~90 m, and a volume of ~14 km^3. Apart from the treated sewage, no other potential sources of anthropogenic nutrient inputs were found in the area of the Inner Gulf. With the secondary treatment process, a removal of organic N through nitrification–denitrification processes was achieved. Since the operation of the biological-grade treatment units (aeration tanks and final settlement) in the second phase, it has been estimated that the organic load has been reduced by 95% (with BOD value of the effluent discharging in the marine environment of 10 mg/L), the total N by 75%, and the total P by 25%. The effects of the second phase on the water quality of the Inner Saronikos Gulf were clearly identified in a 4 or 5-year time frame (Zorpas et al. 2001; Firfilionis et al. 2004; Scoullos et al. 2007; Zeri et al. 2009; Xenarios and Bithas 2009).

The environmental quality of Saronikos Gulf is under study since 1987, within the framework of monitoring programs of the Hellenic Center for Marine Research (HCMR), providing evidence of environmental change. The

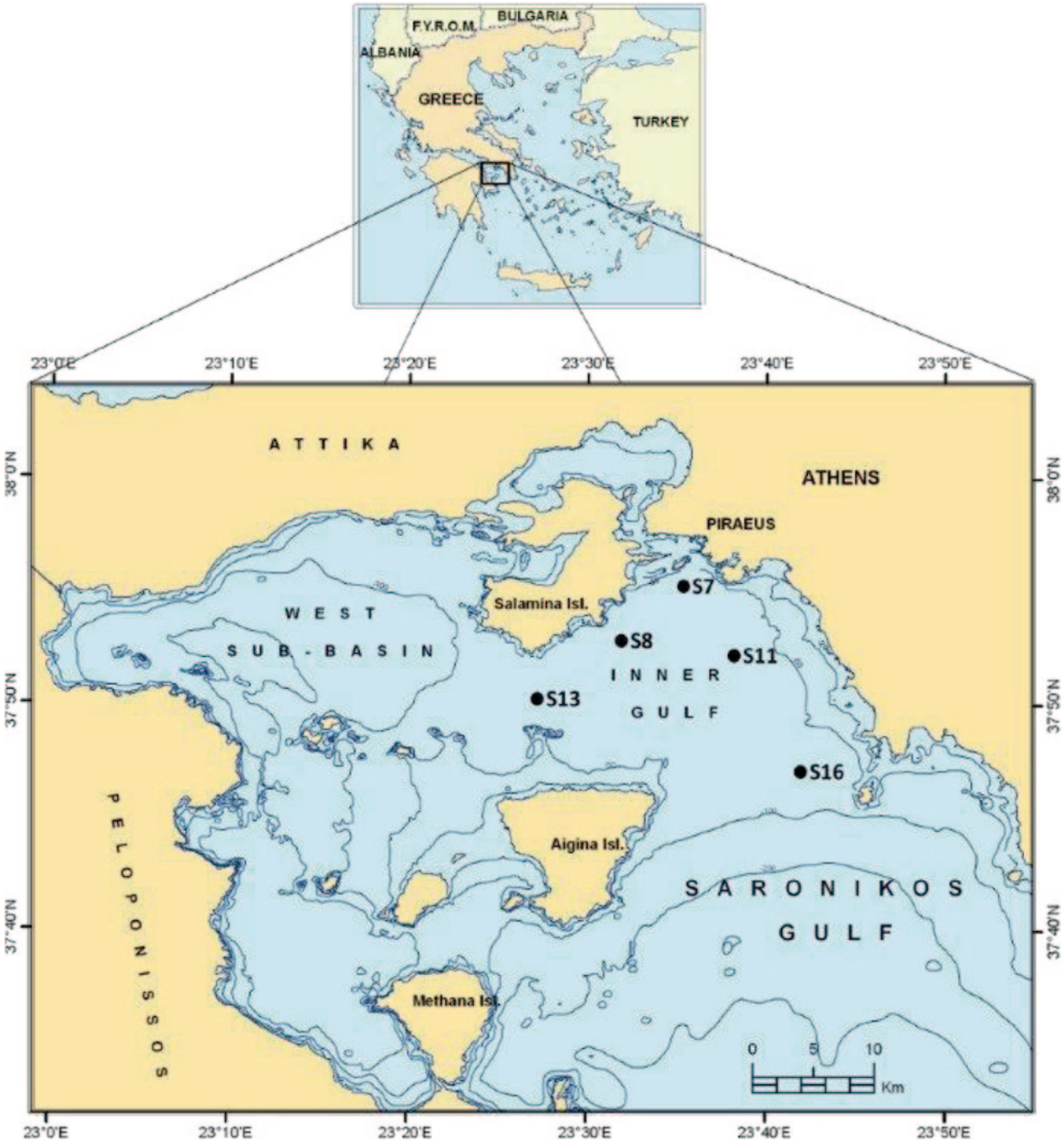

Fig. 10.2 Sampling sites in the inner Saronikos Gulf. Station S7 is located at the Psittalia Sewage outfall

ecosystems of Saronikos Gulf are more manageable after the operation of the sewage treatment plant on the Psittalia Island. In the inner Saronikos Gulf the main nutrient load was presumed to be owing to the sewage effluents. Significant temporal variation of nutrient concentrations showed decreasing trends for nitrate and SRP concentrations, which have revealed an increase in the soluble N:P ratio near the Psittalia sewage treatment plant (Pavlidou et al. 2005; Pavlidou et al. 2008). The operation of the secondary treatment plant since 2004 has affected the ecological statusof the inner Saronikos Gulf.

10.3 Characteristics of the Inner Saronikos Gulf

10.3.1 Field, Laboratory Analysis and Data Assessment

Data were obtained from four to 12 cruises per year from 1987 to 2010 (total 170 cruises), at Saronikos Gulf, using small boats and the research vessels Aegaeo and Filia of the Hellenic Center for Marine Research (HCMR). Five sampling stations in the inner Saronikos Gulf were selected: station S7 at the outfall of the Psittalia sewage pipe; station S8 located 6.81 km southwest of Psittalia Island; station S13 located 15.3 km southwest of Psittalia Island; station S11 located 7.44 km southeast of Psittalia Island; and S16 located 18.1 km southeast of Psittalia Island; Fig. 10.2). At the selected stations seawater samples were collected from surface, 10 m, 20 m, 50 m, 75 m, and near bottom with Niskin bottles, either mounted on a rosette or individually on a hydrowire.

Temperature, salinity, and density in the water column were measured with a CTD profiler (Sea Bird Electronics), which was equipped with pressure, temperature, and conductivity sensors. Before the 1990s measurements were performed with reversing thermometers attached to NIO bottles, whereas, the salinity was determined with an auto lab inductive salinometer.

For oxygen content, samples were taken in sampling bottles with precautionary measures to prevent any biological activity and gas exchanges with the atmosphere (Riley 1975). Samples were analyzed immediately after the collection on board following Winkler method, according to Carpenter (1965a, b).

Water samples for nutrient analyses were collected in 100 mL polyethylene bottles aged with 10% HCl and kept deep-frozen (−20 °C) until their analysis for nitrate, nitrite, silicate, dissolved organic nitrogen, and dissolved organic P (DOP) in the laboratory. Filtered samples from 1987 to1995 analyzed with a TECHNIKON CSM-6 Autoanalyzer, from between 1996 until 1999 with an ALPKEM autoanalyzer and after 1999 to present with a BRAN + LUEBBE II autoanalyzer according to standard methods (Mullin and Riley 1955 for silicate; Strickland and Parsons 1977 for nitrate-nitrite and Murphy and Riley 1962 for SRP).

Ammonium and SRP were measured using Hitachi and Perkin Elmer 20 Lambda and 25 Lambda spectrophotometer (Koroleff 1970 for ammonium and Murphy and Riley 1962 for SRP). ANOVA was used to compare the nutrient concentrations among seasons and sampling stations using SPSS (version 17) statistical program. For rest of the data collected Ocean Data View (ODV) program was used (Schlitzer 2011).

Thematic maps indicating an eutrophication index were produced on the basis of application of interpolation for each parameter for three different periods year 1987–1994, 1995–2004, and 2005–2010. The interpolation method used in this work was Spline with Barriers and a pixel size of 120 m. The analysis was performed in ArcGIS/ArcINFO environment.

10.3.2 Observations on Ecosystem Dynamics

According to Kontoyiannis (2010), the circulation of the Saronikos Gulf has a distinct two-layer structure in the period from late spring to late fall, whereas it is barotropic during the rest of the year (December–March). The treated effluent plume form Psittalia is highly buoyant owing to its large content of freshwater, and it rapidly ascends toward the sea surface. During the stratification period (May–November), the effluent plume is trapped within the seasonal pycnocline whereas during the mixing period (December–April) it reaches the sea surface. Throughout the year, the spreading of the plume is governed by advection caused by the prevailing circulation pattern at the particular layer where the plume floats. Winter temperatures fall to near 13–14 °C, with a complete mixing of the water column in the inner Gulf. The strong thermocline that appears during summer results in a surface-to-bottom temperature change of ~27–15 °C. Higher salinity values are observed in the lower layers owing to Aegean water that spreads north through the southern end of the Gulf where it communicates with the deeper sea. In the presence of a well-developed thermocline (during August–September), the treated plume that is trapped within the pyclnocline in the inner Saronikos Gulf is characterized by relatively lower transparency and lower salinity values (Fig. 10.3).

The sewage plume has relatively high nutrient concentrations (ammonium, SRP, and nitrite; Fig. 10.4). The highest nutrient values during the period of operation of the sewage treatment plant in Psittalia (1994–2010) were recorded at the site of the plume outflow (station S7; Table 10.1). During the warm period (June-October) ammonium concentrations below the pycnocline reached the value of 20 μmol/L (average for the period 1994–2010: 3.26 ± 4.64 μmol/L), whereas, the average SRP concentration in the warm period during 1994–2010 was 0.703 ± 0.658 μmol/L. According to the previous data, nutrient concentrations indicated a significant decreasing shift with distance from the sewageoutfall (station S7), showing that the prevailing water circulation led to the dilution of the effluents in the inner Saronikos Gulf (Pavlidou et al. 2008).

Sewage treatment, deep outflow of the sewage field, and its entrapment below 50 m during the warm season do not favor the development of nitrophilous phytobenthic Chlorophycae in the upper infralittoral zone. As a result the ecological quality of the phytobenthic communities improved since 1994 (primary treatment) and even more after 2004

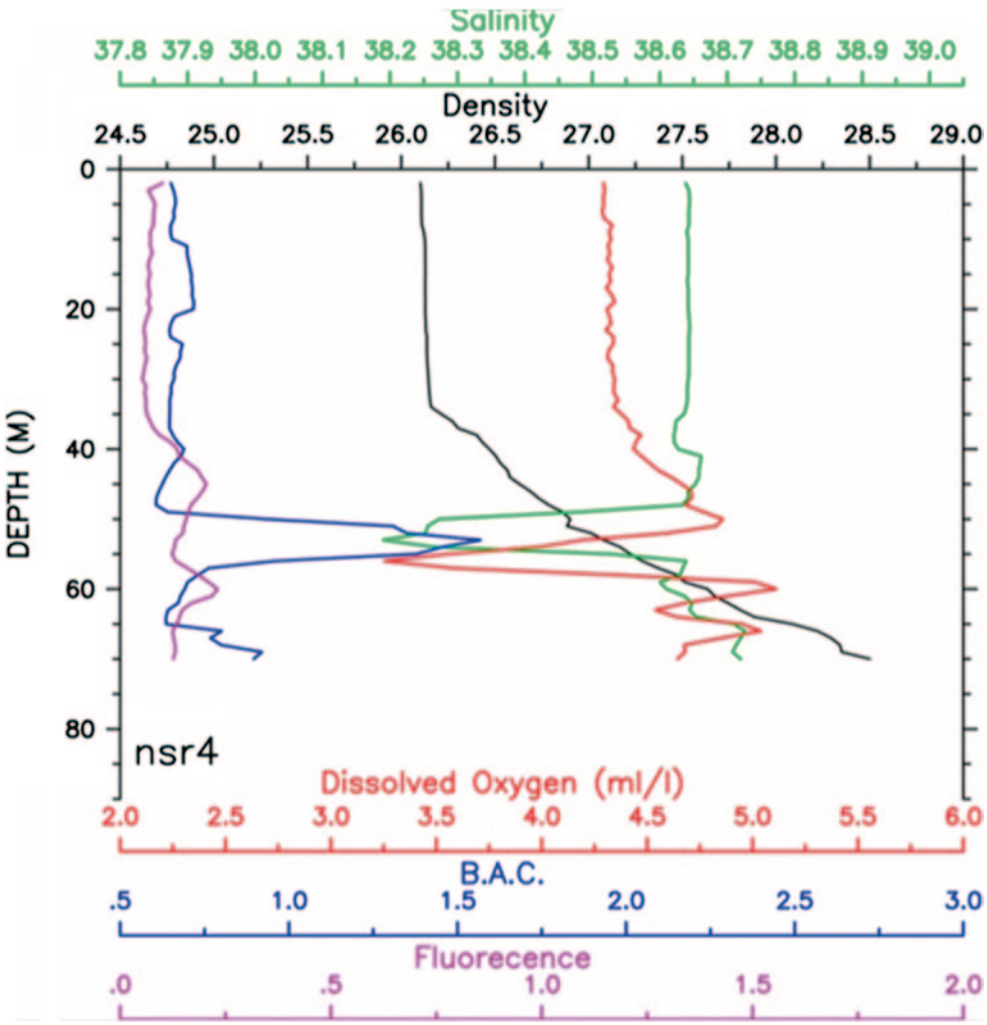

Fig. 10.3 Vertical profiles of physicochemical parameters at station S7 during the warm period

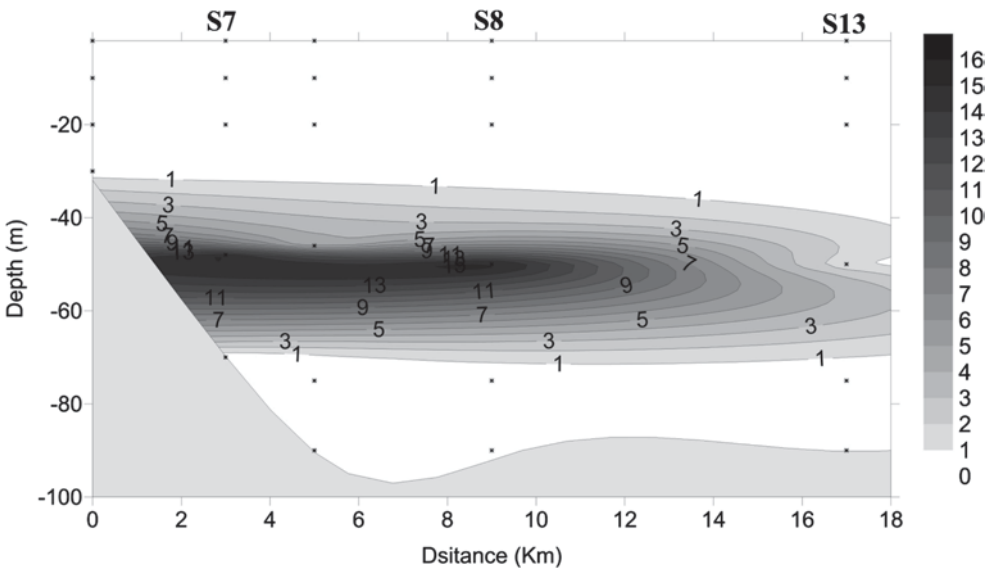

Fig. 10.4 Vertical distribution of ammonium southwest of Psittalia sewage outfall in September 2003

Table 10.1 Average nutrient concentrations and their ratios before and after sewage treatment at station S7

Period	Layers	PO_4^{3-} (μM)	SiO_4^{2-} (μM)	NO_2^- (μM)	NO_3^- (μM)	NH_4^+ (μM)	N:P
Before treatment (1987–1994)	0–20 m	0.42±0.95	1.01±0.38	0.25±0.23	0.68±0.36	0.90±0.96	8.14±3.83
	30–60 m	0.15±0.08	1.18±0.41	0.32±0.23	0.53±0.33	0.44±0.38	9.46±4.35
	Water column	0.24±0.29	1.23±0.44	0.25±0.21	0.61±0.31	0.76±0.56	8.66±3.95
During primary treatment (1995–2004)	0–20 m	0.29±0.25	1.58±0.84	0.23±0.23	0.72±0.49	1.04±1.58	10.6±12.9
	30–60 m	0.56±0.54	1.89±0.80	0.31±0.20	0.73±0.88	1.81±2.90	7.25±6.64
	Water column	0.39±0.23	1.95±0.69	0.30±0.19	0.87±0.51	1.33±1.37	2.37±1.44
During secondary treatment (2005–2010)	0–20 m	0.15±0.11	1.57±0.64	0.12±0.13	0.34±0.33	0.51±0.55	10.8±14.7
	30–60 m	0.28±0.34	1.81±0.93	0.24±0.22	0.81±1.03	1.82±3.89	9.50±7.00
	Water column	0.20±0.13	1.74±0.66	0.21±0.23	0.58±0.42	1.00±1.46	13.1±11.7

(secondary-tertiary treatment) when a significant decline in *Ulva* spp. was observed (Tsiamis et al. 2012). After 1994, soft bottom macroinvertebrate communities, living at 70–90 m depth, showed deterioration very close to the outfall and an improvement with the distance from the discharge point. Elimination of organic load after 2004 by the secondary treatment resulted in the amelioration of the entire area planktonic and benthic communities (Siokou-Frangou et al. 2009). Additionally, the spatial variability of nutrients and particulate organic carbon seems to affect the ecological statusof the inner Saronikos Gulf. According to the classification suggested by the EU Water Framework Directive (2000), ecological quality of the inner Saronikos Gulf of both phytobenthic and macrozoobenthic communities improves with increasing distance from the sewage outfall (Siokou-Frangou et al. 2009) that can vary from poor at station S7 (Bentix index 2.20; Simboura et al. 2005) to moderate at station S8 (Bentix index 2.71) and good at stations S13, S11, and S16 (Simboura et al. 2005; Zenetos et al. 2005; Simboura and Zenetos 2002). The poor trophic status corresponds with the higher mesotrophic conditions indicating "sensitive" ecosystems and leading to eutrophic conditions in future. The good status corresponds with the lower mesotrophic level characterizing nonsensitive areas (Pagou et al. 2002; Simboura et al. 2005).

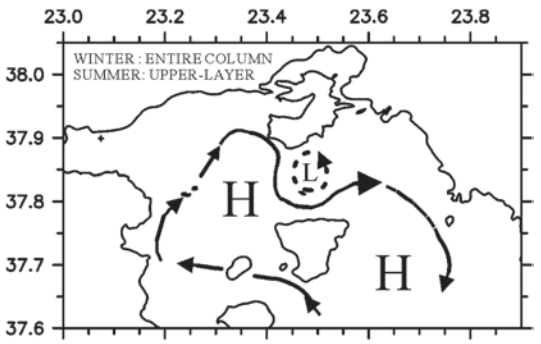

Fig. 10.5 Characteristic circulation pattern in Saronikos Gulf during winter for the entire water column and during summer in the upperlayer, above the seasonal pycnocline (Kontoyiannis, 2010). "The dashed pattern with the 'L' indicates a recurrent (possible) summer feature". The summer deep circulation is reversed relative to the upper-layer circulation

10.3.3 Observations on Hydrography

The circulation in Saronikos Gulf has been described (Kontoyiannis 2010) based on direct current measurements on a seasonal basis and under various wind conditions. It was shown that the circulation of the Saronikos Gulf has a distinct two-layer structure in the period from late spring to summer to late fall, whereas it is barotropic during the rest of the year (December–March). Observations in the Inner Gulf showed that the different wind directions found related to the different circulation patterns of Saronikos Gulf. In summer an anticyclonic and a cyclonic flow exists throughout the Gulf above and below the pycnocline, respectively, whereas, in winter and early spring an anticyclonic flow prevails in the upper ~100 m. In late spring-early summer cyclonic and anticyclonic flow occurs in the upper (~0–40 m) and deeper (~60–100 m) layers, respectively (Fig. 10.5). Throughout the year, the spreading of the plume was governed by advection caused by the prevailing circulation pattern at the particular layer where the plume floats.

The profiles (Fig. 10.3) show typical seasonal variations of dissolved oxygen, chlorophyll, salinity, density, and turbidity expressed as beam attenuation coefficient (B.A.C.) at station S7. The higher values of beam attenuation coefficient are indicative of lower water transparencies. In the presence of a well-developed thermocline, the treated plume was trapped in the pycnocline at S7, shown by the lower transparency and lower salinity values near ~50 m. Generally, in the inner Saronikos Gulf, lower salinity values were observed in the deeper layers owing to the influence of Aegean water coming into the inner Gulf from the south open boundary. During the winter mixing period, the plume ascends to the sea surface, occupying a surface layer approximately 20–30 m thick.

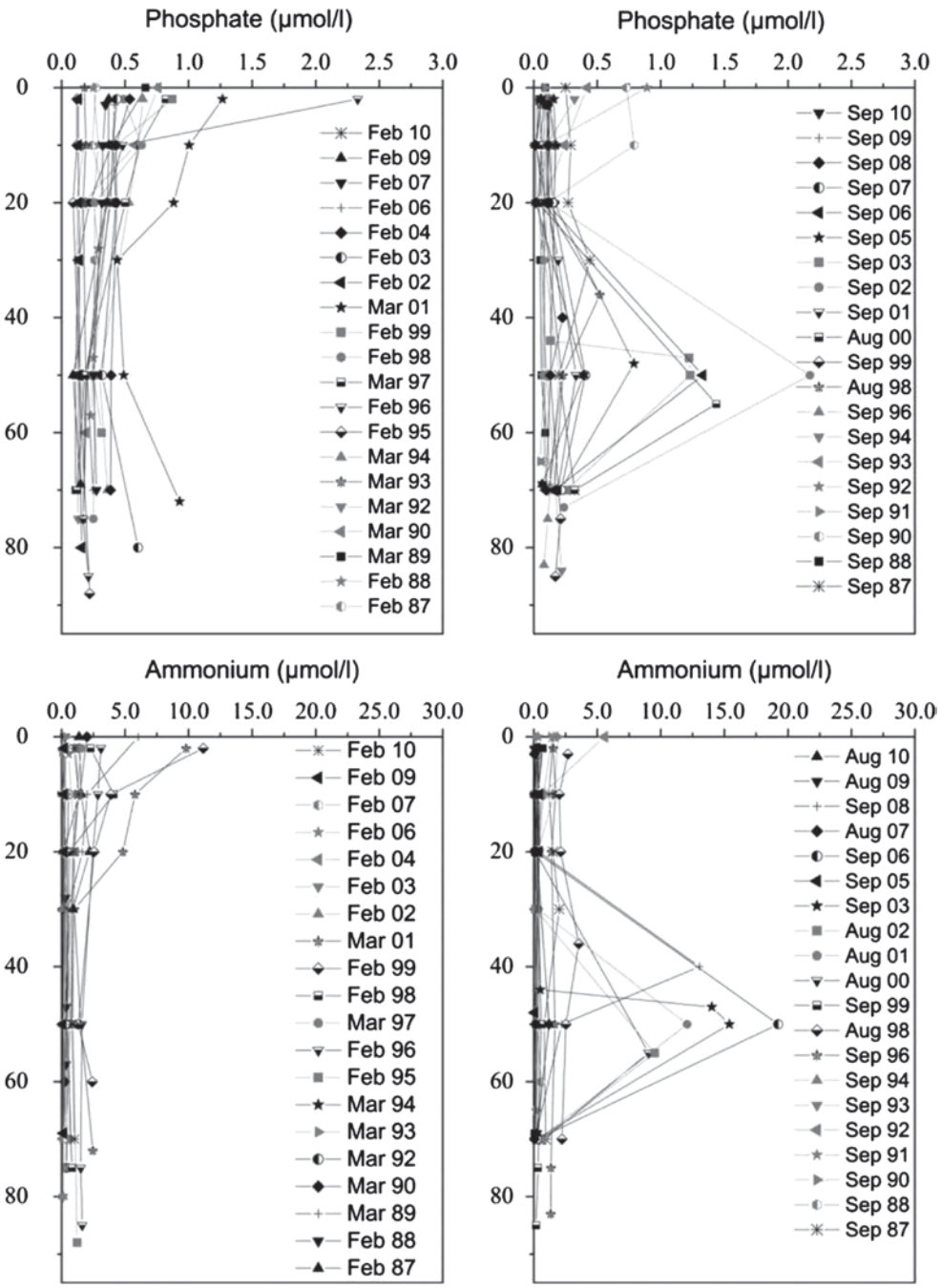

Fig. 10.6 Vertical distribution of phosphate and ammonium at the sewage outfall (station S7) in cold (February or March/non-stratified) and warm (August or September/stratified) periods during 1987–2010

10.3.4 Observations on Dissolved Oxygen and Nutrients of the Water Column

Dissolved oxygen (DO) and inorganic nutrient data of 12 months samplings during November 2009–October 2010, as well as from the 170 cruises obtained during 1987–2010, used to describe the oxygen and nutrient dynamics of the inner Saronikos Gulf in phase with stratification of the water masses and the sewage discharge from the Psittalia Island sewage treatment plant.

Depth profiles of nutrients at the Psittalia outfall showed that during the warm/stratified period, SRP and ammonium concentrations increased markedly into and/or below the pycnocline, directly related to the sewage plume discharging from the Psittalia Island sewage treatment plant through the pipe at 63-m depth. This was prominent only after September 1996. Before that period an increase of nutrients in the surface layer (0–20 m) was sometimes observed (Figs. 10.6 and 10.7). After 2004, where the secondary stage of treatment operated on Psittalia Island, a significant decrease in

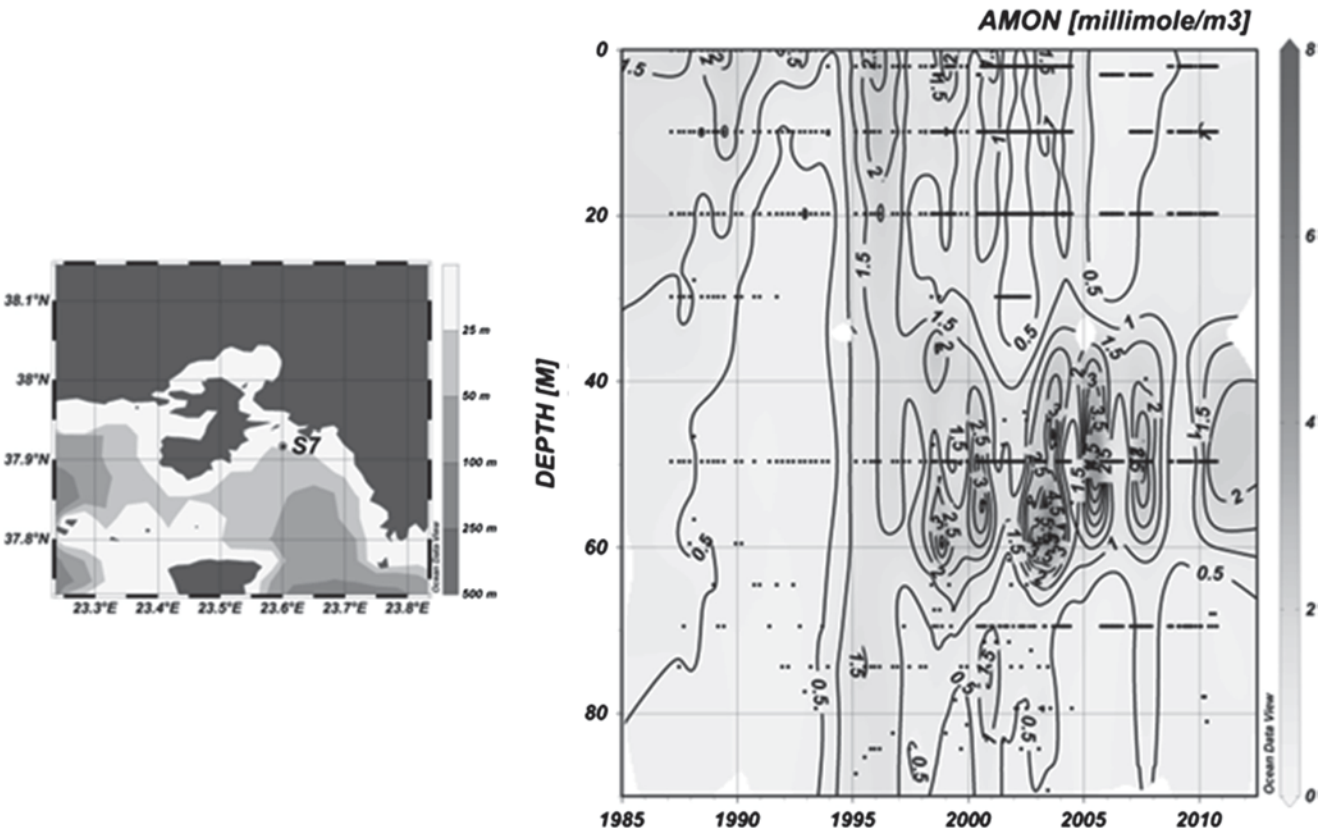

Fig. 10.7 Vertical distribution of ammonium at station S7 during the period 1987–2010

SRP and ammonium concentrations within and below the pycnocline was observed.

In winter (February/March), nutrient concentrations at station S7 remained almost stable with depth, with relatively higher values in the surface layer. Soluble reactive phosphorus and ammonium concentrations in the surface layer (2–20 m) ranged between 0.09 and 2.33 μM (average value 0.416 ± 0.232 μM) and from 0.50 to 11.2 μM (average value 1.53 ± 1.72 μM), respectively. In the layer from 30 m to the bottom, SRP and ammonium concentrations were lower and ranged between 0.09 and 0.929 μM (average value 0.240 ± 0.121 μM) for SRP and from 0.07–2.45 (average value 0.615 ± 0.539 μM) for ammonium. The DIN:SRP ratio (DIN stands for the sum of nitrate + nitrite + ammonium) was 7.53 in the surface layer and 8.59 in the layer from 30 m to the bottom.

During the warm August/September of 1987–1994 SRP concentrations in the surface layer ranged between 0.040 and 0.890 μM (average value 0.241 ± 0.185 μM). Whereas during 1995–2010 SRP concentration was, lower and ranged between 0.012 and 0.173 μM (average value 0.094 ± 0.057 μM). Similarly, ammonium concentrations ranged between 0.160 and 5.580 μM (average value 0.838 ± 0.682 μM) during the period 1987–1994, whereas, during 1995–2010 ammonium concentrations were lower (average value 0.547 ± 0.681 μM). After the operation of the sewage treatment, the surface layer of station S7 is not affected by the sewage effluents, as the sewage plume is trapped within or below the pycnocline and cannot reach the surface layer. The layer at depth of 30 m on the bottom was affected by the sewage plume showing elevated SRP and ammonium concentrations for the period 1995–2010 (ammonium: 0.05–19.2 μM, average value 2.31 ± 3.06 μM; SRP: 0.067–2.173 μM, average value 0.422 ± 0.348 μM). Before the operation of the sewage treatment nutrient concentrations were significantly lower (ammonium: 0.16–2.00 μM, average value 0.422 ± 0.355 μM; SRP: 0.01–0.440 μM, average value 0.117 ± 0.086 μM). DIN:SRP ratio in the layer from 30 m to the bottom did not show significant variation between the two study periods (12.9 before the operation of the sewage treatment and 13.3 after the operation of the sewage treatment) showing that inorganic nitrogen and SRP increased almost with the same rate. Nitrogen was found as a limiting factor for phytoplankton growth. On the contrary, a significant increase of the DIN:SRP ratio was observed in the surface layer between the two periods during summer. DIN:SRP increased from 5.9 for the period 1987–1995 to 19.6 for the period 1995–2010. This increase of DIN:SRP ratio is owing to the significant decrease of SRP in the surface layer after the discharge of the sewage effluents at 63 m depth, whereas, DIN concen-

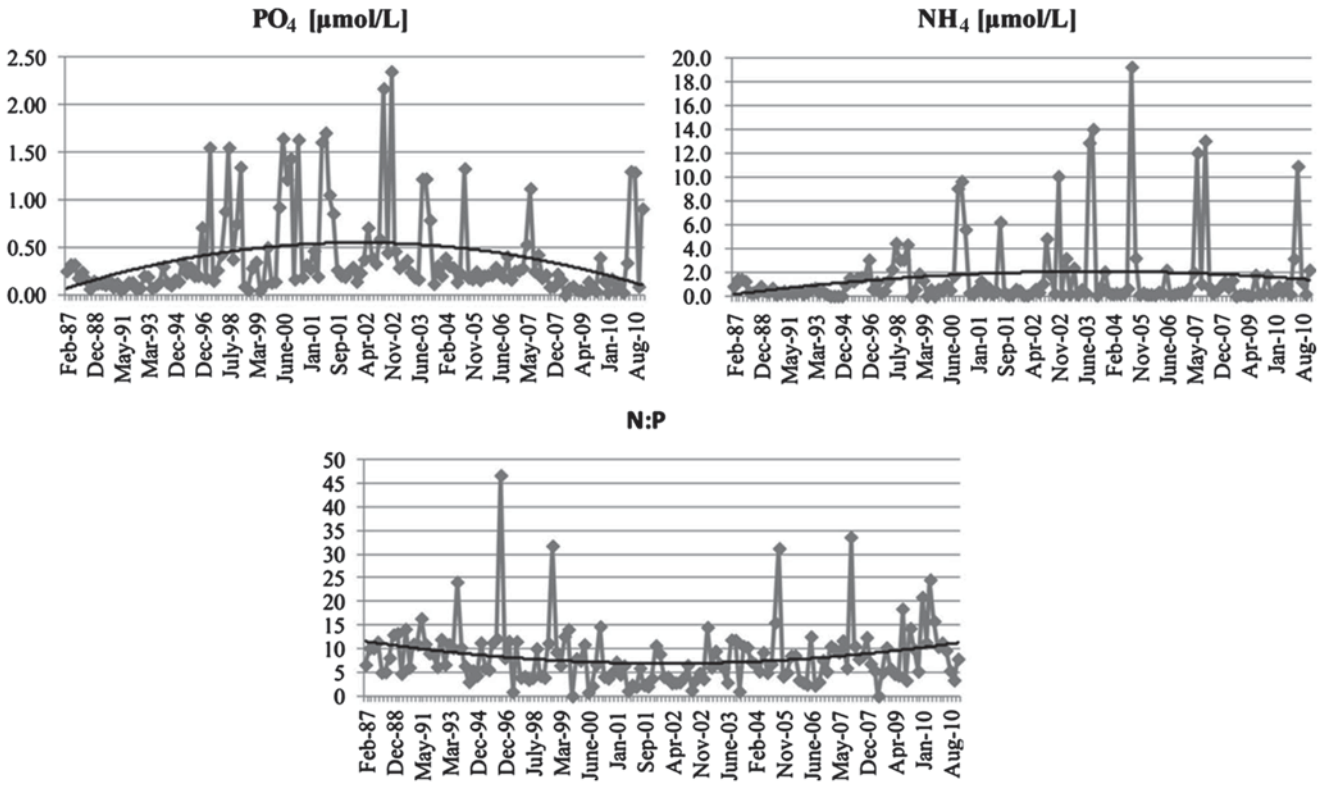

Fig. 10.8 Temporal variability of phosphate, ammonium and N:P ratio within the layer 30–60 m at Psittalia outfall (station S7) during 1987cline. During the period 1987–1994 the effluents from Athens city were discharged untreated north eastern of Psittalia at the surface layer of the water column; during 1995–2004 the sewage plume was discharged in the Inner Saronikos Gulf (S7 station, 63 m depth) primarily treated; during 2005–today the sewage plume is discharged in the Inner Saronikos Gulf after a secondary treatment

trations remained constant (average values: 1.39 ± 0.819 μM and 1.30 ± 1.284 μM, respectively). The shift of the surface layer from N-limitation to P-limitation indicates a change in the trophic status of station S7. Seasonal variability of nutrient limitation is discussed below.

Historical data from the period 1987–2010 confirm the increase of nutrient concentrations, especially of SRP and ammonium, in the layer within and/or below the pycnocline (30–60 m) after the operation of the sewage treatment plant. Whereas DIN:SRP ratios decreased from 9.46 (average value for the period 1987–1994) to 7.25 (average value for the period 1995–2004), after that an increasing trend was observed. This likely reflected an upgrade of the environmental quality in this layer related to the secondary treatment of sewage (Fig. 10.8; Pavlidou 2012). However, the average DIN:SRP ratio was calculated below the theoretical value of Redfield, indicating N-limitation within and/or below the pycnocline at the sewage discharge (station S7). Before sewage treatment plant was operational, the average concentrations of SRP and nitrite in the surface layer of station S7 were 0.42 μmol/L and 0.25 mol/L, respectively. The Ammonium was 0.90 μmol/L and after the secondary sewage treatment, the average SRP, nitrite, and ammonium concentrations reduced to 0.15 μmol/L, 0.12 μmol/L and 0.51 μmol/L, respectively. On the contrary, within and/or below the pycnocline, SRP and ammonium concentrations increased considerably (Table 10.1).

Significant seasonal variation in nutrient concentrations of station S7 was observed before and after the primary and secondary sewage treatment. More specifically, using data from 1987 to 2010, the mean values of nutrient concentrations at station S7 calculated for two periods: before (1987–1994) and after (1995–2010) the operation of the sewage treatment plant (Table 10.2). Typically, the highest concentrations occurred in spring or early summer. During 1987–1994, $NO_3^- + NO_2^-$ showed high concentrations in early spring, whereas, secondary peaks were observed in August and November/December. Soluble reactive phosphorus, silicate, and ammonium seasonal variations before the operation of the treatment plant followed the same pattern, showing high concentrations in summer (August) and in late autumn (November). Minima observed in April. During the discharging of the sewage plume in the inner Saronikos (S7, 1995–2010), the seasonal variation of $NO_3^- + NO_2^-$ also showed higher concentrations in winter/early spring period, whereas silicate did not show a clear seasonal variation. Ammonium and SRP are good indicators of sewage discharge. Indeed, they were very similar to each other in seasonal vari-

Table 10.2 Seasonal average nutrient concentrations and their ratios before and after sewage treatment, at station S7. Period A: before treatment (1987–1994), B: during primary treatment (1995–2004), C: during secondary treatment (2005–today)

	PO_4^{3-} (μM)	SiO_4^{2-} (μM)	NO_2^- (μM)	NO_3^- (μM)	NH_4^+ (μM)	N:P
Winter A	0.187±0.117	1.272±0.283	0.403±0.191	0.663±0.160	0.866±0.720	11.8±2.54
Winter B	0.415±0.210	1.849±0.536	0.469±0.172	0.924±0.426	1.617±1.090	8.62±3.96
Winter C	0.341±0.185	1.883±0.614	0.381±0.174	0.861±0.420	1.266±1.024	8.49±3.86
Spring A	0.322±0.213	1.015±0.216	0.356±0.328	0.869±0.417	0.966±1.043	8.27±3.54
Spring B	0.306±0.235	1.535±0.687	0.191±0.141	0.801±0.389	0.597±0.461	10.3±10.7
Spring C	0.141±0.071	1.405±0.518	0.088±0.043	0.292±0.214	0.750±0.786	12.7±9.63
Summer A	0.259±0.188	0.942±0.331	0.098±0.096	0.572±0.418	1.096±1.255	5.57±2.71
Summer B	0.127±0.055	1.104±0.360	0.054±0.024	0.349±0.184	0.538±0.568	13.0±11.7
Summer C	0.106±0.064	1.441±0.477	0.055±0.027	0.147±0.098	0.411±0.326	12.3±15.3
Autumn B	0.591±0.404	1.621±0.946	0.198±0.159	0.666±0.290	2.597±2.900	6.21±4.42
Autumn C	0.115±0.015	1.240±0.240	0.084±0.076	0.307±0.080	0.556±0.437	7.19±6.21

ation at station S7 during 1995–2010 with two main peaks in summer (June–August), late autumn (November) and March (Fig. 10.9). Minimum concentrations of nitrate and nitrite in spring related to the biological activity. The spring enhances chlorophyll values and consumption of nitrates by phytoplankton for biomass formation, whereas minimum was recorded during September–October. Similarly, in Elefsis Bay (north of Saronikos Gulf), SRP, silicate, DIN, and ammonium concentrations at the near-bottom waters were usually maximal in September, but elevated concentrations were found during July to November and minimum in April (Pavlidou et al. 2010).

Concerning the different forms of dissolved inorganic nitrogen (DIN), all forms (NO_3^-, NO_2^- and NH_4^+) were present, but after 1996 a significant increase of the NH_4^+/DIN (%) from 38 to almost 80 was observed in the layer from 30 to 60 m during the warm period, with a parallel decrease of NO_3^-/DIN (%) from 44 to 17.

The mean Si:DIN ratio did not show significant seasonal variation (average value for the period 1987–2010: 1.16±0.23; for the period 1987–1994: 0.93±0.22; for the period 1995–2010: 1.23±0.30). A higher Si:NO_3^- value was recorded in September (average value for the period 1995–2010: 5.20). On the other hand, the Si:P mean ratio showed significant seasonal variation with high values in April and May (11.4 and 13, respectively, for the period 1987–2010 and 13 and 14.1 for the period 1995–2010) and low mean values (5.8 for the period 1987–1994 and 5.6 for the period 1995–2010) in March. The Si:P ratio calculated for the period 1987–1994 exhibited high values in November (15.9) that decreased significantly in January (4.64). Our results showed that silicate concentrations in the water column of station S7 for the period 1995–2010 has increased compared with the 1987–1994 period.

The atomic Si:N:P ratio of marine diatoms is about 16:16:1 in a nutrient-replete ecosystem (Redfield 1958; Brzezinski 1985; Xu et al. 2008). Deviation from the Redfield ratio indicates the potential for N, P, or Si limitation of phytoplankton growth. In our assessment of stoichiometric limitations, we have calculated Redfield ratiosfollowing Pavlidou et al. (2004) and Xu et al. (2008) to predict:

1. N limitation occurs when DIN:SRP < 16 and DIN:Si < 1
2. P limitation occurs when DIN:SRP > 16 and Si:SRP > 16
3. Si limitation occurs when DIN:Si > 1 and Si:SRP < 16

Plots of the atomic Si:SRP against DIN:SRP ratios in the water column of station S7 indicate that the nutrients are potentially limiting the phytoplankton biomass. The data points in the upper left quadrant (DIN:SRP < 16:1) are indicative of N limitation, in the upper right quadrant are indicative of P limitation, and of Si limitation in the lower left quadrant (Fig. 10.10). The quadrant with the most data points indicates frequent occurrences of potential limitation of a particular nutrient. The calculation of the ratios DIN:SRP, Si:SRP and Si:DIN in the entire water column of station S7 (n = 801) during the period 1987–2010 (both warm and cold periods included) indicated stoichiometric P-limitation by about 7%. Furthermore, the data indicated significant probable N-limitation (47%), whereas Si-limitation was 40%. During summer (June-September) N-limitation calculated to be 52%, whereas P-limitation and Si-limitation was 9% and 31%, respectively. In winter (December–March) P-limitation was not probable (4%), whereas a shift to Si-limitation (56%) was observed, while N-limitation in winter was 33%. It seems that Si concentrations in the water column of station S7 might affect the dynamics of phytoplankton. Additionally, in spring (April–May) N-limitation was 53%, whereas P-limitation and Si-limitation calculated at 16% and 30% respectively. In November, N-limitation was 49%, whereas Si-limitation was 42% and P-limitation was not found (Table 10.3). According to the calculations, a general shift from Si-limitation to N-limitation before and after the operation of the sewage treatment plant observed at station S7. Before the sewage treatment, Si-limitation of 60–65% in winter and spring seemed to determine the trophic status of station S7, whereas after the operation of the secondary sewage treatment, significant probable N-limitation recorded.

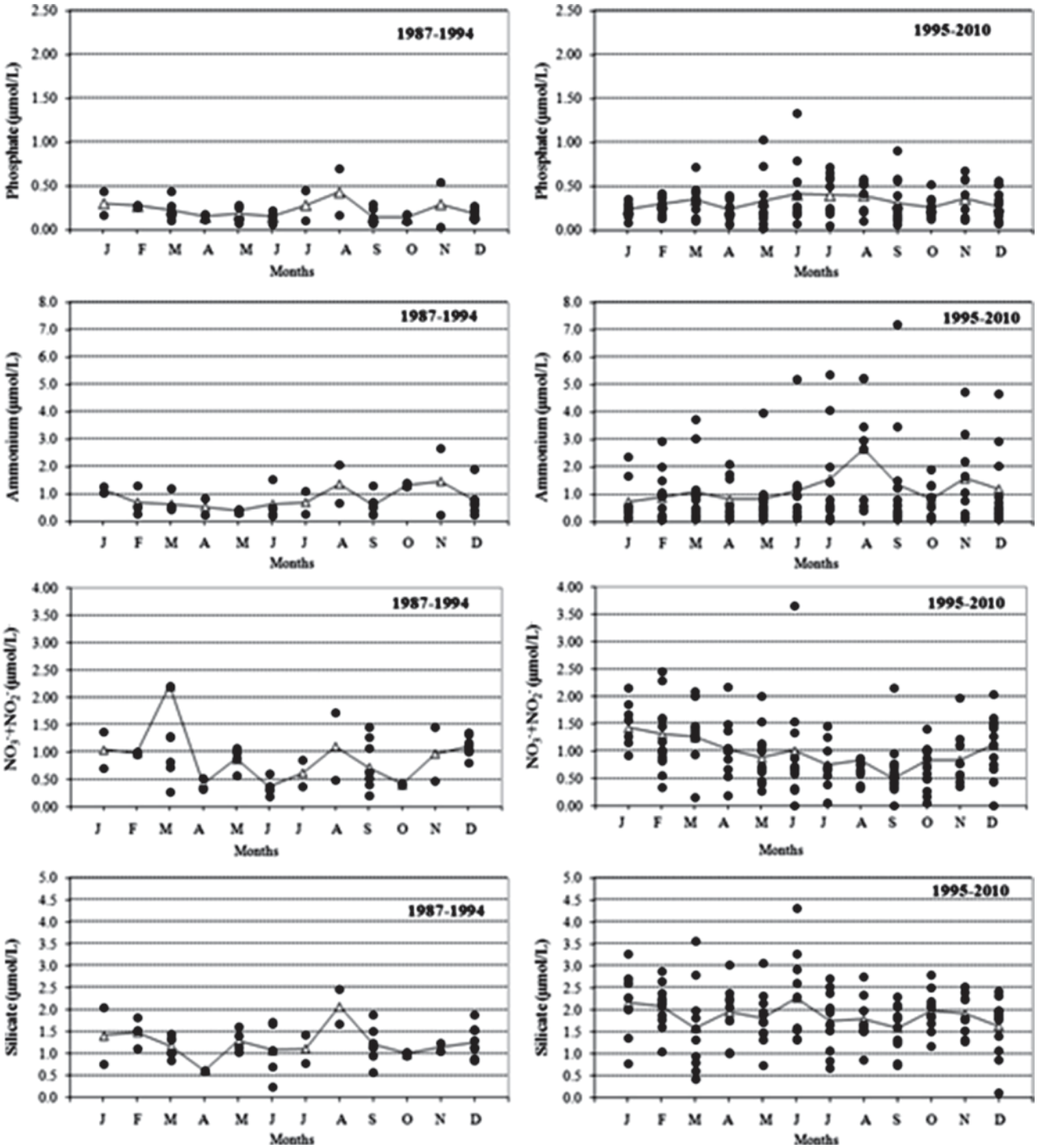

Fig. 10.9 Monthly variations of nutrients at station S7 for the period before the operation of the treatment plant (1987–1994) and after the operation of the treatment plant at Psittalia (1995–2010). Triangles connected by lines indicate the mean of each cruise period

This shift from Si-limitation to N-limitation during almost 25 years suggests changes in the marine ecosystem and the phytoplankton community, probably owing to the removal of N during the secondary sewage treatment. The nutrient concentrations for the period 2005–2010 gave a mean Si:DIN atomic ratio of 1.5, with an increasing trend with distance southeast from the sewage outfall, whereas at station S8 which is located southwest of Psittalia Island outfall the mean Si:DIN ratio was slightly decreased. Decreasing Si:DIN ratio may exacerbate eutrophication by reducing the potential for diatom growth, in favor of noxious flagellates (Alonso-Rodriguez et al. 2009, Pavlidou et al. 2004). However, this is not

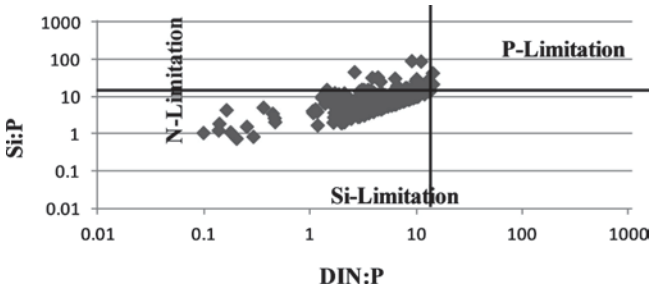

Fig. 10.10 Scatter diagram of atomic nutrient ratios for the water column of station S7 for the period 1987–2010. DIN, P and Si represent dissolved inorganic nitrogen ($NO_3^- + NO_2^- + NH_4^+$), P, and Si. Stoichiometric (=potential) limitation for DIN, P, and Si is indicated by the number of data points in the various quadrants

the case of the inner Saronikos Gulf since the Si:DIN ratio is higher than the theoretical one. Yet the DIN:SRP and Si:SRP ratios at station S7 were significantly reduced, which may lead to increased blooms in the future.

Monthly data of nutrients and their ratios as well as of chlorophyll-a for station S7 for the period November 2009–October 2010 showed significant temporal variations (Fig. 10.11). During this period N-limitation was probable (58%), whereas Si-limitation and P-limitation were calculated at 24% and 18%, respectively. Significant variation in nutrient ratios observed during 2009–2010. In winter 47% N-limitation was observed, whereas there were equal percentages of P-limitation (27%) and Si-limitation (27%). In spring a shift from N-limitation (30%) to P-limitation (40%) was observed, whereas in summer and autumn N-limitation was probable as it was calculated to be 75% in both seasons. A peak of nutrient concentrations occurred in summer. Phytoplankton data at station S7 for the period 2009–2010 indicated that diatoms were the predominant phytoplankton group, and the potentially toxic diatom *Pseudo-nitzschia* was present during the year (up to 30,080 cells/L) (Pagou et al. 2011). The decreased concentrations of silicate during spring (higher percentage of Si-limitation) probably reflected the development of the spring diatom bloom (Fig. 10.10; Pagou et al. 2011).

Most responses occurred in the immediate vicinity of the sewage discharge and rapidly decreased with distance. However, all the study stations of the inner Saronikos Gulf (6–18 km from the sewage outfall) had ratios Si:DIN > 1, DIN:SRP < 16 and Si:SRP < 16, with the exception of stations S11, S13, and S16, which during 2005–2010 had Si:SRP ratios of 21.7, 20.9, and 32.9, respectively (Table 10.4).

10.3.5 Eutrophication Scale

The ecological quality status (according to the classification suggested by the EU Water Framework Directive 2000) of phytobenthic and macrozoobenthic communities improved with the increasing distance from the sewage outfall, varying from poor to high (Fig. 10.12a, b; Siokou-Frangou et al. 2009; Simboura et al. 2005). According to Pavlidou (2012), the classification based on nutrient concentration scale of Karydis (1999) applied to the Greek coastal areas indicate that the Psittalia sewage outfall (station S7) is characterized as eutrophic for nitrate and higher mesotrophic for SRP and ammonium. The inner Saronikos Gulf, which receives sewage from the Psittalia outfall, is characterized as higher mesotrophic for nitrate and lower mesotrophic for ammonium and SRP. The water mass circulation plays an important role in the nutrient dynamics of the outer Saronikos Gulf, which is oligotrophic for ammonium, lower mesotrophic for SRP, and upper mesotrophic for nitrate.

Table 10.5 shows the ecological quality of the study area based only on SRP, nitrate, and ammonium concentrations, before (a), during the primary sewage treatment (b) and during the secondary sewage treatment (c). According to Karydis (1999) four levels of classification are used in the eutrophication scale: eutrophic, higher mesotrophic, and oligotrophic. These levels could be considered as corresponding to the five categories of environmental status as defined by the European Water Framework Directive (WFD): eutrophic for bad, higher mesotrophic for poor and moderate, lower mesotrophic for good, and oligotrophic for high. According to this scale, an area is characterized as: oligotrophic, with nutrient concentrations < 0.07 μM for SRP; < 0.62 μM for nitrate and < 0.55 μM for ammonium; lower mesotrophic, with concentrations 0.07–0.14 μM for SRP; 0.62–0.65 μM for nitrate and 0.55–1.05 μM for ammonium; higher mesotrophic,

Table 10.3 Nutrient limitation calculated seasonally for the following different periods: 1987–2010; 1987–1994: before the operation of the sewage treatment plant in Psittalia; 1995–2004: during the primary treatment of the sewages; 2005–2010: during the secondary treatment of sewages

Season/period	1987–2010			1987–1994			1995–2004			2005–2010		
Limitation	N	P	Si	N	P	Si	N	P	Si	N	P	Si
Winter	33%	4%	56%	25%	2%	65%	29%	5%	59%	57%	4%	28%
Spring	53%	16%	29%	20%	20%	60%	55%	12%	33%	61%	16%	16%
Summer	52%	9%	31%	45%	3%	35%	53%	8%	33%	56%	16%	26%
Autumn	49%	0%	42%				47%	0%	53%	53%	0%	16%
All year	47%	7%	40%	33%	3%	51%	45%	6%	44%	58%	11%	25%

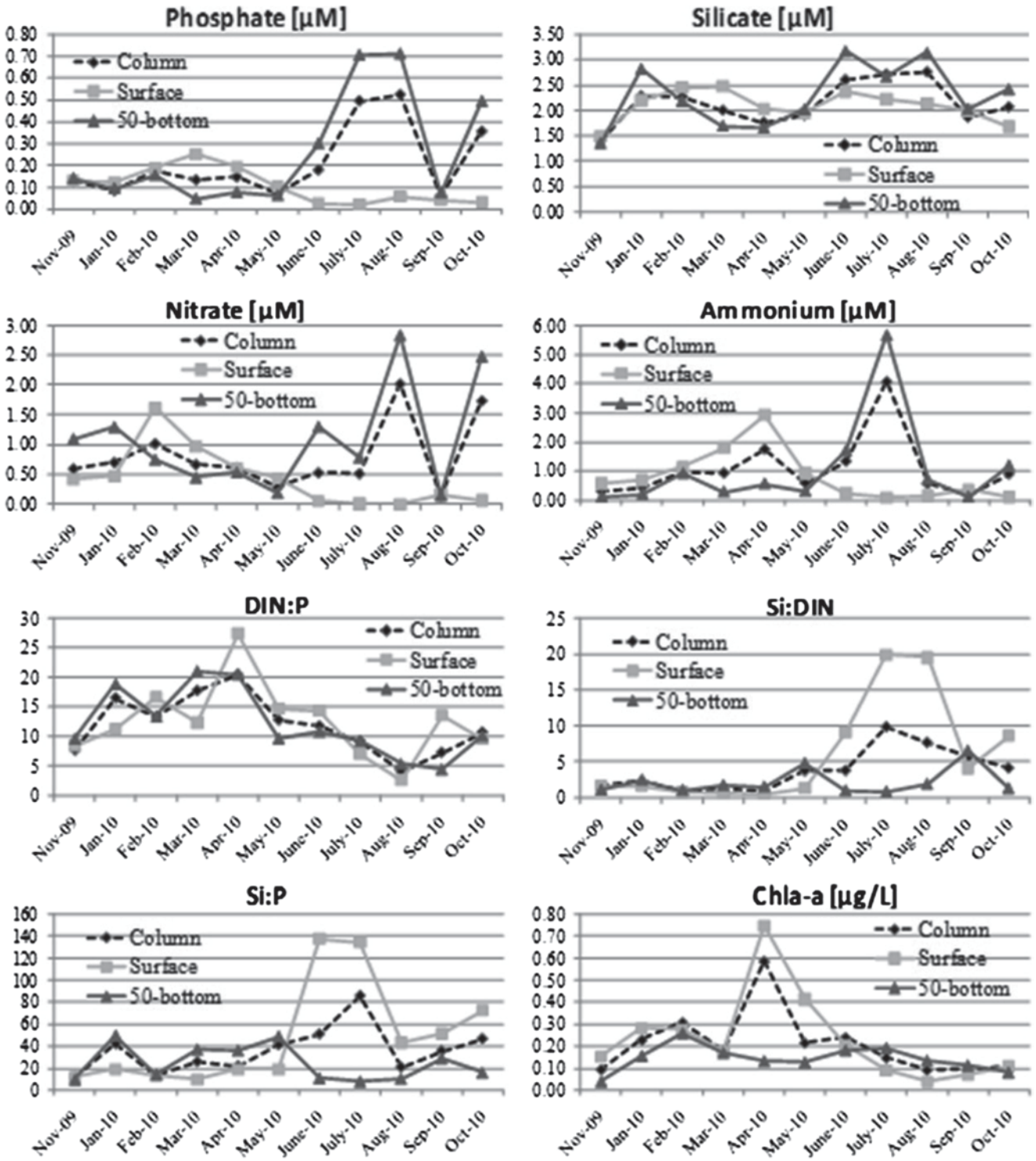

Fig. 10.11 Monthly variations of nutrients, their ratios and chl-a at station S7 for the period November 2009–October 2010

with concentrations 0.14–0.68 μM for SRP; 0.65–1.09 μM for nitrate and 1.05–2.2 μM for ammonium and eutrophic, with concentrations higher than 0.68 μM for SRP; 1.19 for nitrate and 2.20 for ammonium. Additionally, the ecological scale for the period 2009–2010 was applied to the inner Saronikos Gulf based on nutrient and chlorophyll-values. According to Karydis (1999) the area is characterized as: oligotrophic, with chl-a concentration <0.1 μg/L; lower mesotrophic, with concentrations between 0.1 and 0.6 μg/L; higher mesotrophic, with concentrations 0.6–2.21 μg/L and eutrophic, with concentrations higher than 2.21 μg/L.

Table 10.4 Mean integrated nutrient concentrations and their ratios for the water column before and after preliminary and secondary sewage treatment at different stations of the Inner Saronikos Gulf located at the sewage discharge (S7) and in a distance southwest (S8, S13) and southeast (S11, S16) from Psittalia. All nutrient concentrations are expressed in μM

	PO_4	SiO_4	NO_2	NO_3	NH_4	DIN:P	Si:P	DIN	Si:DIN	$Si:NO_3$
S7										
1987–1994	0.243	1.228	0.250	0.605	0.755	8.664	8.041	1.562	0.934	2.611
1995–2004	0.390	1.951	0.295	0.867	1.328	7.025	6.623	2.371	1.033	2.821
2005–2010	0.202	1.739	0.205	0.583	0.997	9.333	13.13	1.784	1.541	4.111
S16										
1987–1994	0.107	1.023	0.160	0.382	0.354	9.613	12.56	0.849	1.451	3.806
1995–2004	0.129	1.657	0.172	0.536	0.312	11.03	18.56	1.006	2.028	4.904
2005–2010	0.075	1.398	0.090	0.355	0.261	12.65	32.89	0.706	2.794	8.533
S11										
1987–1994	0.122	1.013	0.194	0.491	0.440	9.968	10.30	1.092	1.090	3.249
1995–2004	0.201	1.813	0.256	0.835	0.441	10.22	12.01	1.460	1.382	2.627
2005–2010	0.112	1.535	0.136	0.516	0.307	10.50	21.68	0.920	2.135	5.101
S13										
1987–1994	0.114	1.367	0.197	0.697	0.440	11.11	13.63	1.167	1.411	2.125
1995–2004	0.197	1.895	0.234	1.084	0.441	10.11	11.46	1.680	1.365	2.119
2005–2010	0.108	1.721	0.114	0.734	0.307	12.55	20.91	1.171	1.748	4.129
S8										
1998–2004	0.249	2.009	0.250	1.127	0.256	7.771	9.574	1.623	1.330	1.955
2005–2010	0.157	1.734	0.156	1.007	0.333	10.50	13.22	1.496	1.374	3.590

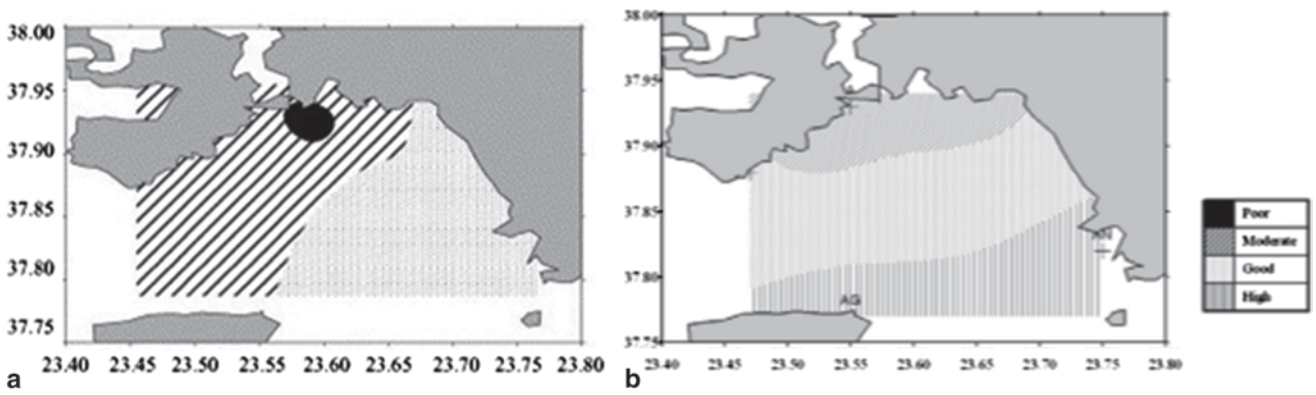

Fig. 10.12 **a** Ecological Quality Status (EcoQ) of macro-invertebrate communities in Saronikos Gulf according to the classification suggested in the WFD (from Simboura et al. 2005). **b** Ecological Quality Status (EcoQ) of macrophyte communities in Saronikos Gulf according to the classification suggested in the WFD

Taking into account the whole water column and the annual mean values, station S7 is characterized as higher mesotrophic for SRP before and after the operation of the sewage treatment, whereas interesting changes of the trophic characterization for nitrate and ammonium were observed. It seems that after the operation of the primary sewage treatment the marine environment in the vicinity of the sewage outfall became more eutrophic, as it received a great amount of effluents for the first time. After the operation of the secondary sewage treatment, a shift to a better trophic status was achieved for nitrate and ammonium. However, higher mesotrophic conditions for SRP indicate a sensitive marine area, as it can be eutrophic in the future (Pagou 2005). It seems that this is not the case for S7 station as a decreasing trend for SRP after 2005 has been detected (Fig. 10.8).

Taking into account the whole water column and the annual mean values of nutrients and chlorophyll-a for the period 2009–2010, station S7 is characterized as higher mesotrophic for SRP, nitrate, and ammonium and lower mesotrophic for chlorophyll-a. Station S11, which is located 7.4 km southeast of the Psittalia outfall, is characterized as oligotrophic for SRP, nitrate, and ammonium and lower mesotrophic for chlorophyll-a. Station S8, which is located almost at the same distance (~7 km) southwest of the Psittalia outfall, seems to be a more eutrophic station, as it is characterized as lower mesotrophic for SRP and chlorophyll-a,

Table 10.5 Trophic classification of the stations in the Inner Saronikos Gulf based on nutrient mean annual values for the following different periods: 1987–1994: before the operation of the sewage treatment plant in Psittalia; 1995–2004: during the primary treatment of the sewages; 2005–2010: during the secondary treatment of sewages

	For phosphate	For nitrate	For ammonium
S7			
1987–1994	HM	OL	LM
1995–2004	HM	HM	HM
2005–2010	HM	OL	LM
S16			
1987–1994	LM	OL	OL
1995–2004	LM	OL	OL
2005–2010	LM	OL	OL
S11			
1987–1994	LM	OL	OL
1995–2004	HM	LM	OL
2005–2010	LM	OL	OL
S13			
1987–1994	LM	HM	OL
1995–2004	HM	HM	OL
2005–2010	LM	HM	OL
S8			
1998–2004	HM	HM	OL
2005–2010	HM	HM	OL

OL Ologotrophic; *HM* Highly mesotrophic; *LM* Low mesotrophic

higher mesotrophic for nitrate, and oligotrophic for ammonium. Stations S16 and S13, 18 km and 16 km southeast and southwest of Psittalia, respectively, are characterized as oligotrophic for SRP, nitrate, and ammonium and lower mesotrophic for chlorophyll-a. It seems that station S8 more affected by the effluents from Psittalia than station S11, further supported by the circulation in inner Saronikos Gulf favors the dispersion of effluents to the southwest, rather than to the south east of the outfall. Thus a synthetic trophic condition presentation was produced for the inner Saronikos Gulf based on all available environmental parameters according to Pavlidou et al. (2010; Figs. 10.13a–c).

On the thematic maps shown in Fig. 10.13a–c three categories of eutrophication index (EI) were used:

1. Oligotrophic
2. Mesotrophic
3. Eutrophic

EI calculated according to the following formula:

$$EI = 0.279*C_{SPR} + 0.261*C_{NO_3} + 0.296*C_{NO_2} + 0.275*C_{NH_4} + 0.214*C_{Chla\text{-}a}$$

For production of the thematic maps shown in Fig. 10.13a–c data of nitrate, nitrite, ammonium, and SRP concentrations were used and applied to the EI formula, whereas for the production of the thematic map shown in Fig. 10.14 data of nitrate, nitrite, ammonium, SRP, and chlorophyll-a concentrations were applied to the EI formula.

The eutrophication index for station S7 characterized as mesotrophic during the three study periods (Fig. 10.13), whereas, a shift from oligotrophy to mesotrophy observed at stations S11 and S13 between the periods 1987–1994 and 1995–2005. During the period 2005–2010 stations S11 and S13 characterized as oligotrophic, indicating a significant improvement in ecological status. Station S16 was oligotrophic during the three periods, whereas station S8 was mesotrophic for both the periods 1998–2004 and 2005–2010. Only stations S7 and S8 characterized as mesotrophic after the operation of the secondary sewage treatment, also confirmed by the thematic maps for the period 2009–2010 (Fig. 10.14). After the primary sewage treatment the mesotrophic area covered almost all of the inner Saronikos Gulf (except station S16), whereas, after the secondary sewage treatment the mesotrophic area was significantly restricted.

High nutrient concentrations and low DO values (<3.00 mL/L) were detected near the bottom of the inner Saronikos Gulf, as the biochemical result of the oxidation of the organic matter which is carried by the wastewater effluents into the inner Saronikos Gulf. This was more prominent near the bottom of the stations located southwest and in a distance from the Psitallia sewage plant (~6–14 km), indicating that the organic matter which is carried by the wastewater plume followed the prevailing circulation and finally decomposed at a distance from the pipe, resulting in the DO decrease. It seems that there is a systematic variation pattern of the DO values throughout a year, with an increase during February–March, because of the homogenization of the water column and the oxygenation of the deep layers. The investigation of fecal sterols in the sediments (coprostanol values, coprostanol/cholesterol, and coprostanol/coprostanol + cholestanol ratios) confirms the sewage dispersion pathways. According to these results, although the whole area in a distance ~14 km from the outlet is contaminated by human wastes, the sediments in a direction southwest of Psittalia were more seriously affected than in the southeast direction (Pavlidou et al. 2012).

10.3.6 Statistical Analysis

Statistically significant changes in SRP, ammonium, and nitrate concentrations were observed between the three periods at station S7. Significantly, higher nutrient concentrations recorded after the operation of the primary sewage treatment plant. It seems that the high amount of the primarily treated effluents that discharged in the inner Saronikos Gulf lead to the significant increase of nutrient concentrations in the water column of the inner Saronikos Gulf (Table 10.6).

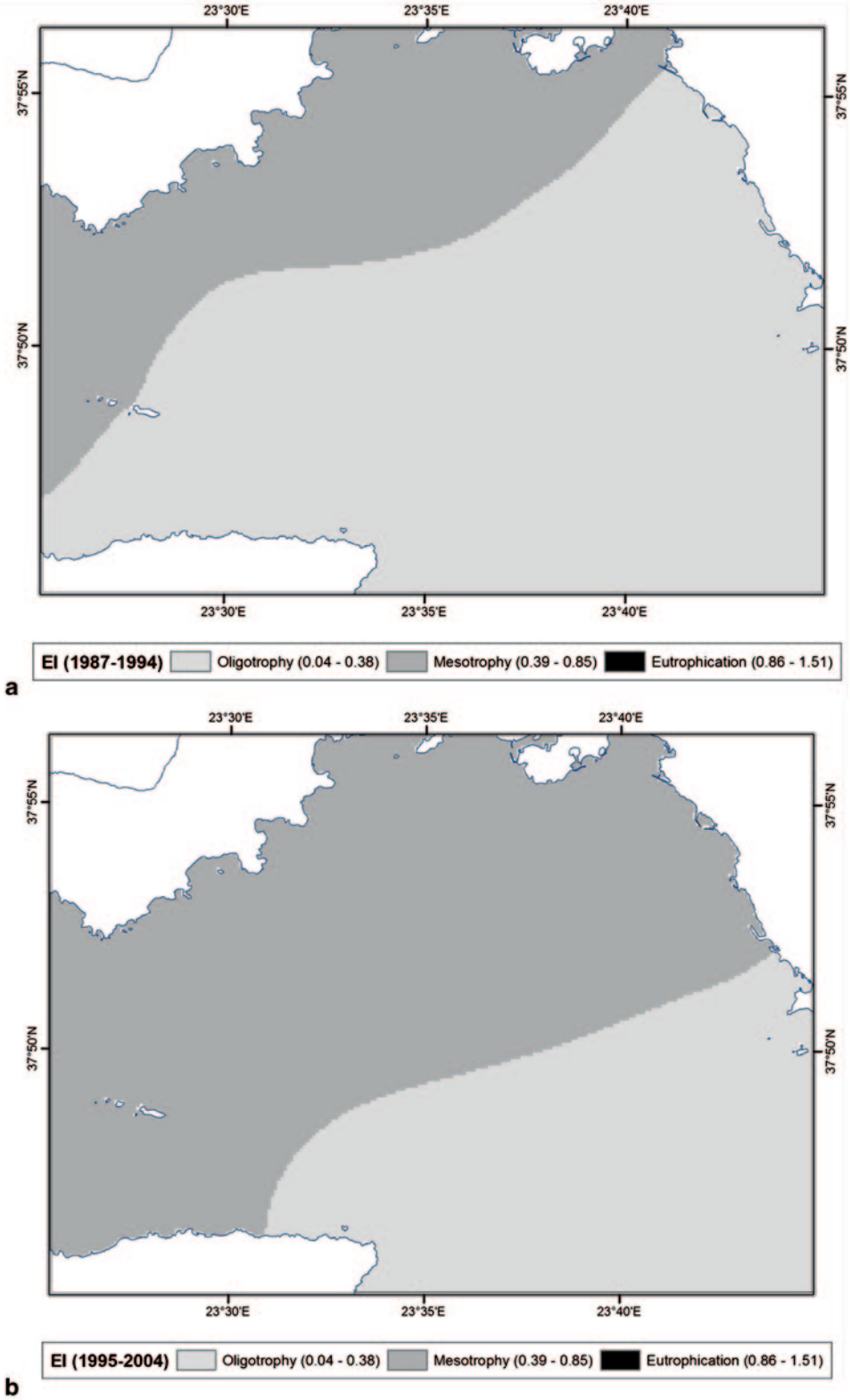

Fig. 10.13 **a, b** Thematic maps showing the eutrophication index in the inner Saronikos Gulf according to the synthesis of all examined parameters (nitrate, nitrite, ammonium, phosphate) for the three study periods

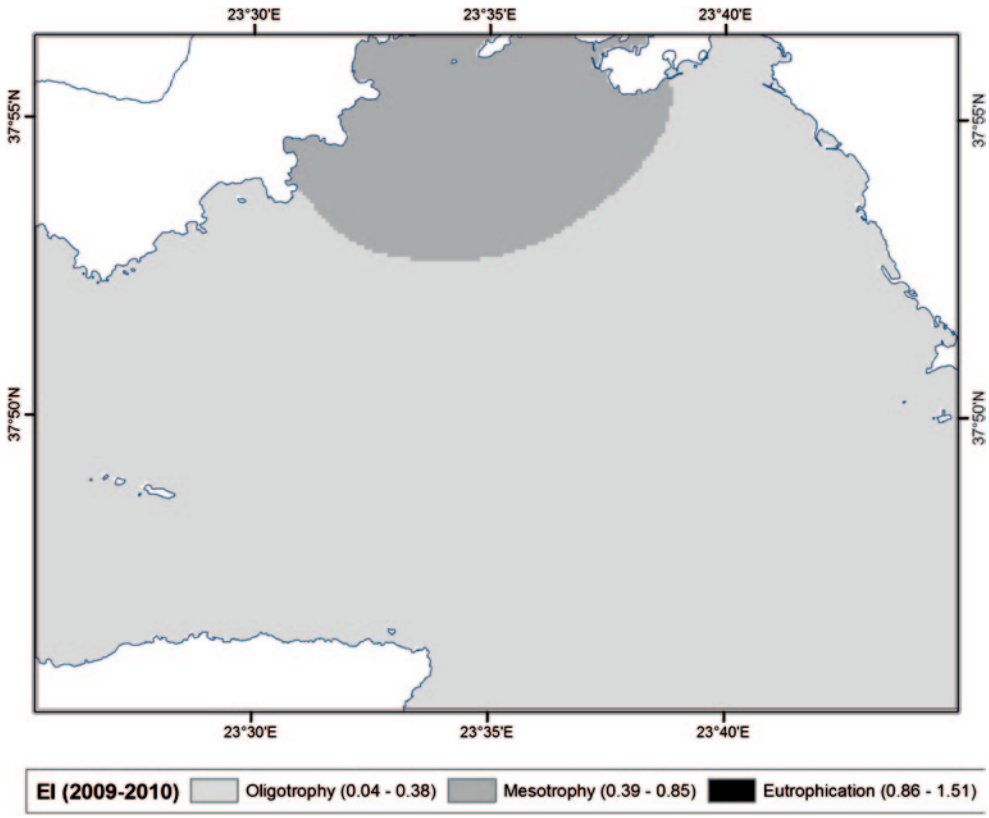

Fig. 10.14 Thematic maps showing the eutrophication index in the inner Saronikos Gulf according to the synthesis of all examined parameters (nitrate, nitrite, ammonium, phosphate, chlorophyll a) for the period 2009–2010

Table 10.6 Results of one way anova performed in order to compare the nutrient concentrations among the three periods of measurements, A: 1987–1994, B: 1995–2004, C: 2005–2010. The *P* values in italics indicate significant mean difference at the 0.05 level

Parameter	PO_4			NO_3			NH_4			N:P		
S7												
Periods	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C
P values	*0.020*	0.660	*0.000*	0.050	0.966	*0.020*	*0.070*	0.646	0.515	0.121	0.739	*0.013*
S11												
Periods	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C
P values	*0.000*	0.886	*0.000*	*0.000*	0.951	*0.000*	1.000	0.343	0.224	0.986	0.945	0.978
S13												
Periods	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C
P values	*0.000*	0.932	*0.000*	*0.000*	0.952	*0.009*	0.673	0.994	0.609	0.759	0.625	0.101
S16												
Periods	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C
P values	0.368	0.188	*0.030*	*0.046*	0.922	*0.014*	0.731	0.316	0.634	0.703	0.257	0.802
S8												
Periods	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C	A-B	A-C	B-C
P values			*0.000*			0.421			0.158			*0.012*

10.4 Conclusions

Significant changes in nutrient dynamics were observed after the operation of the primary sewage treatment plant with higher nutrient concentrations recorded in the inner Saronikos Gulf. It seems that the high amount of the primarily treated effluents that discharged in the inner Saronikos Gulf led to the significant increase of nutrient concentrations in the water column nearby to the sewage outfall. After 2005, when the secondary sewage treatment operated, a general decrease in nutrient concentrations in the inner Saronikos Gulf was observed.

A shift from Si-limitation to N-limitation was observed at station S7, based on 25 years of data, suggesting changes

in the marine ecosystem and the phytoplankton community, which is probably related to the removal of nitrogen during the secondary sewage treatment.

The eutrophication index applied to the study area for the three study periods showed that station S7 characterized as mesotrophic during all periods, whereas, a shift from oligotrophy to mesotrophy was observed at stations S11 and S13 between the periods 1987–1994 and 1995–2005. During the period 2005–2010 stations S11 and S13 were characterized as oligotrophic, indicating a significant improvement in ecological status of the stations. Station S16 was oligotrophic during the three periods, whereas station S8 characterized as mesotrophic for both the periods 1998–2004 and 2005–2010. It is noteworthy that only stations S7 and S8 characterized as mesotrophic after the operation of the secondary sewage treatment. A deterioration of station S8, which is located 7 km southwest of the Psittalia outfall, was observed after the operation of the sewage treatment plant. Where relatively lower DO concentrations were recorded near the bottom of station S8 (in some cases lower than 3.00 mL/L) as a biochemical result of the oxidation of the organic matter carried by the wastewater effluents into the Inner Saronikos Gulf.

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Eutrophication Impacts on Salt Marshes Natural Metal Remediation

11

Isabel Caçador and Bernardo Duarte

Abstract

Salt marshes are a very important part of the estuarine ecosystem, with an important role within the biogeochemical cycles, being areas of high primary production, which also contribute importantly as shoreline stabilizers. Besides, periodical tidal flooding of salt marshes also causes the transport of significant quantities of pollutants, which tend to accumulate in the marsh ecosystem. Therefore, salt marshes are considered to be important sinks namely of heavy metals. Their important role has been recently admitted by the inclusion of these ecosystems in the European Water Framework Directive (WFD). Multiple services of wetlands and its value are already well known, such as excess contaminant and nutrient removal. Nitrogen concentrations in salt marsh sediments have been increasing, mostly owing to the anthropogenic activities increase in the estuarine surrounding areas. This leads to an increase in the halophyte biomass and an apparent reduction in the phytoremediation capacity. Although eutrophication processes apparently reduce the natural remediation capacity of the marsh toward the estuary, it also allows an increase in the potential sink capacity and a reduction of the contaminated detritus export into the estuarine system and into the food web.

Keywords

Eutrophication · Halophyte · Phytoremediation · Salt marshes

11.1 Salt Marshes: Valuable Ecosystem Services Providers

Salt marshes have great ecological value, in terms of nutrient regeneration, primary production, habitat for wildlife, and as shoreline stabilizers. Periodic tidal flooding of salt marshes provides large quantities of pollutants to the marsh ecosystem. Thus, salt marshes are considered to be important sinks for pollutants (Caçador et al. 1993, 1996, 2007; Davy 2000; Prange and Dennison 2000). Salt marshes are natural sites for deposition of heavy metals in estuarine systems (Caçador et al. 1993, 2009; Doyle and Otte 1997; Williams et al. 1994; Duarte et al. 2010). When located near polluted areas, these ecosystems receive large amounts of pollutants from industrial and urban wastes that either drift downstream within the river flow or are the direct result of waste dumping from nearby industrial and urban areas (Caçador et al. 2009). When metals enter salt marshes they spread along with the tides and periodic floods and interact with soil and the biotic community (Suntornvongsagul et al. 2007). Most salt marsh plants accumulate large amounts of metals in their aerial and below ground organs (Caçador et al. 2000). Among these are the most common plants of southern European salt marshes: *Sarcocorniafruticosa, S. perennis, Halimioneportulacoides* and *Spartinamaritima*. Their ability to phytostabilize those contaminants in the rhizosediment is an important aspect of self-remediative processes and biogeochemistry in this eco-

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Fig. 11.1 Nitrogen concentration (%) in two different salt marshes of Tagus estuary, from 1960 to 2000 (average ± standard deviation)

system (Caçador et al. 1996; Sundby et al. 1998; Weis and Weis 2004).

11.2 Estuarine Eutrophication

One of the greatest problems in coastal waters is eutrophication. Salt marshes import inorganic nutrients and export organic nutrients. As tidal water flows through salt marshes, plants, bacteria, and algae produce or transform the organic matter of the food chain that supports fish and shellfish populations (Teal and Howes 2000). While salt marshes modify the forms of the principal plant nutrients N and P, some of the pathways result in removal of nutrients from biologically active systems. Flooding with seawater leads to an input of inorganic and organic substances into the marsh (Rozemaet al. 2002). Nitrogen is removed primarily either by (1) being trapped in refractory organic matter that contributes to marsh maintenance through accretion, or (2) by loss to the atmosphere (as N_2) through denitrification. Coastal marshes tend to be nitrogen limited. With increasing nitrogen supply, marshes show greater primary productivity by both grasses and algae. Unlike some coastal systems, salt marshes can withstand very large additions of nitrogen without severe damage (Teal and Howes 2000). In addition, estimates of the size of the N-pool do not always indicate the availability of nitrogen to plants. The increasing soil nitrogen content with salt marsh age indicates that the salt marsh soil acts as a sink for N. Some other studies focused on the N-content of salt marsh compartments have been published (Caçador et al. 2007; Sousa et al. 2008; Rozema et al. 2002) (Fig. 11.1).

11.3 Halophyte Phytoremediation Capacity

Salt marsh plants play an important role in the dynamics of the estuarine ecosystem. Plants act as sediment traps, facilitating the retention of suspended estuarine particulates with

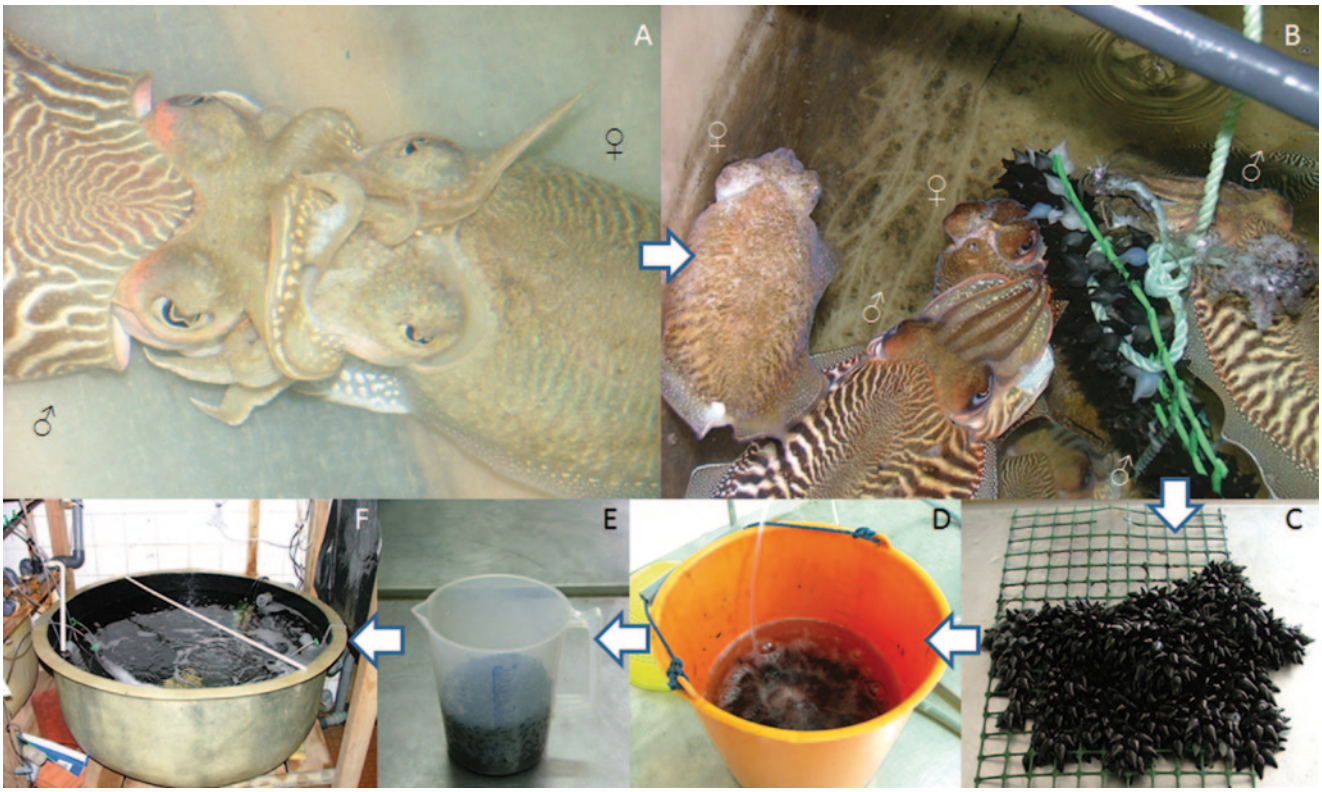

Fig. 11.2 Biomass production (Kg ha^{-1} y^{-1}) and root:shoot ratio (R/S) among the different nitrogen fertilization treatments (average ± standard deviation)

their associated metals, and influencing retention and accumulation processes of metals in salt marsh sediments (Salgueiro and Caçador 2007). The metal concentrations in salt marsh sediments are often related to contamination of the coastal environment. Tagus salt marshes were enriched substantially with the heavy metals Pb, Zn, Cd, and Cu. Although concentrations of other heavy metals have been measured in these sediments (Duarte et al. 2008, 2009, 2010; Caçadoret al. 2009) their enrichment factors were rather low compared to Pb, Zn, Cd, and Cu. Halophytes take up heavy metals from sediments through their roots and alter the sediment biogeochemistry. This uptake is influenced by several factors such as: metal availability, root activity (Duarte et al. 2007), sediment biogeochemistry (Duarte et al. 2008), microorganism activity (Duarte et al. 2009), and plant species (Caçadoret al. 2009; Duarte et al. 2010).

11.4 Eutrophication and Primary Production

In salt marsh halophytes the quantity of below ground biomass is often much larger than the amount of above ground material (Gross et al. 1991; Caçadoret al. 1999). Plants in physiologically stressed environments, such as salt marshes, have been assumed to have high below ground biomass (Waisel 1972; Groenendijk and Vink-Lieavaart 1987). In well-established salt marshes, the intense competition for nutrients results in increased allocation of biomass to root material (Gross et al. 1991). High root:shoot biomass common in halophyte species has been considered to be indicative of adaptive mechanisms, with a need for greater root surface under unfavorable soil conditions (Lana et al. 1991). Many factors, such as elevation, interstitial salinity, nitrogen availability, oxygenation of the root system, and anthropogenic factors, have been reported to have important roles in biomass production (Lana et al. 1991). Nitrogen fertilizations field experiments can give good insights about the halophyte biomass allocation versus nutrient availability. Although the above ground biomass does not appear to have a positive correlation with the nitrogen availability, the halophyte nutrient harvesting organs show a clear trend, upon N-fertilizer application. Tilman's allocation model states that plants that allocate their biomass to roots are best competitors when below ground resources are abated (Tilman 1988). On the other hand, best competitors for light are those plants that allocate very large fractions of their biomass in above ground organs. In this case, N application seemed to have stimulated the root production in order to increase the N-harvesting capacity by the halophyte. On the other hand, this increase harvesting is not reflected in the above ground

Table 11.1 Heavy metal concentrations (μg/g DW) in the above and below ground organs upon different fertilization application (average ± standard deviation)

	Control	200 Kg N ha^{-1} y^{-1}	600 Kg N ha^{-1} y^{-1}
Above ground			
Co	7.34 ± 1.63	5.96 ± 1.00	6.38 ± 1.34
Cd	2.87 ± 0.67	3.55 ± 0.86	1.59 ± 0.29
Cu	5.59 ± 0.93	5.82 ± 2.38	4.15 ± 1.02
Zn	39.20 ± 7.56	778.52 ± 12.46	67.14 ± 15.08
Pb	5.58 ± 0.93	19.99 ± 6.52	18.90 ± 5.47
Below ground			
Co	10.73 ± 4.11	15.53 ± 2.08	13.88 ± 4.35
Cd	15.95 ± 6.06	12.85 ± 3.96	11.71 ± 3.03
Cu	271.76 ± 50.70	207.86 ± 73.67	208.94 ± 27.40
Zn	1200.81 ± 193.61	1037.00 ± 275.45	872.09 ± 75.55
Pb	860.04 ± 280.55	756.87 ± 140.53	752.98 ± 94.30

biomass, indicating a clear excess in nitrogen that is not followed by an increase in the primary production mechanisms, thus revealing a low nitrogen efficiency use (Fig. 11.2).

11.5 Eutrophication Versus Phytoremediation

Although the overall trend increasing root biomass and with this the major organic sink of heavy metals, their concentration in roots seem to be rather depleted upon application of increasing N doses (Table 11.1). Overlooking the concentrations in the above ground tissues there seemed to be an increase in the concentration of the metals upon N application. This is directly related with the higher translocation rate verified in the areas were N fertilization was applied, rather than with an increased metal uptake. This is an indication that there was no interaction between N supply and metal bioavailability.

Nevertheless, this metal concentration reduction, assuming root as the most important biological sink, is also resultant of an artifact that can mislead to a wrong conclusion. As stated before, the N application resulted in an increase in the biomass, especially in the root biomass. Therefore, the reduction of metal concentration verified is due not to a reduced metal harvesting ability, but to a dilution of the elements in a larger amount of biomass. More interesting, if the metal pools are observed instead of the metal concentration on a dry weight basis, the opposite trend can be verified (Figs. 11.3 and 11.4). The increase in biomass production, probably owing to a higher nutrient harvesting, also lead to a higher incorporation of metals in the newly formed biomass. This way, overlooking metal pools there can be observed an increase in the metal pool in the root compartment upon N application (Fig. 11.3). This can also be observed within the above ground biomass (with the exception of Cu) and it is concomitant with the high translocation rates already verified (Fig. 11.4).

11.6 Conclusion

Nitrogen concentrations in salt marsh sediments have been increasing, mostly owing to intensification of the anthropogenic activities in the estuarine surrounding areas. One of the more evident consequences of this increase is the halophyte biomass increase as response to this N fertilization. Simultaneously with this biomass increase, there is an apparent decrease in the phytoremediation ability by the halophytes, with a decrease in the metal concentrations in its tissues, mostly owing to a dilution of these toxic elements in the newly formed biomass. Although this could be interpreted as a reduction of the ecosystem services provided by the salt marsh, reducing the estuarine remediation capacity, a closer look will also reveal a positive effect of this process. With the biomass increase there will be an increase in the biological sink capacity of the marsh, allowing higher amounts of metals to be sequestrated by the halophyte root system. Also, considering the natural exports of biomass mostly owing to senescence, the amounts of exported metals into the surrounding estuarine water column, are greatly reduced.

Although eutrophication processes apparently reduce the natural remediation capacity of the marsh toward the estuary, it also allows an increase in the potential sink capacity and a reduction of the contaminated detritus export into the estuarine system and into the food web.

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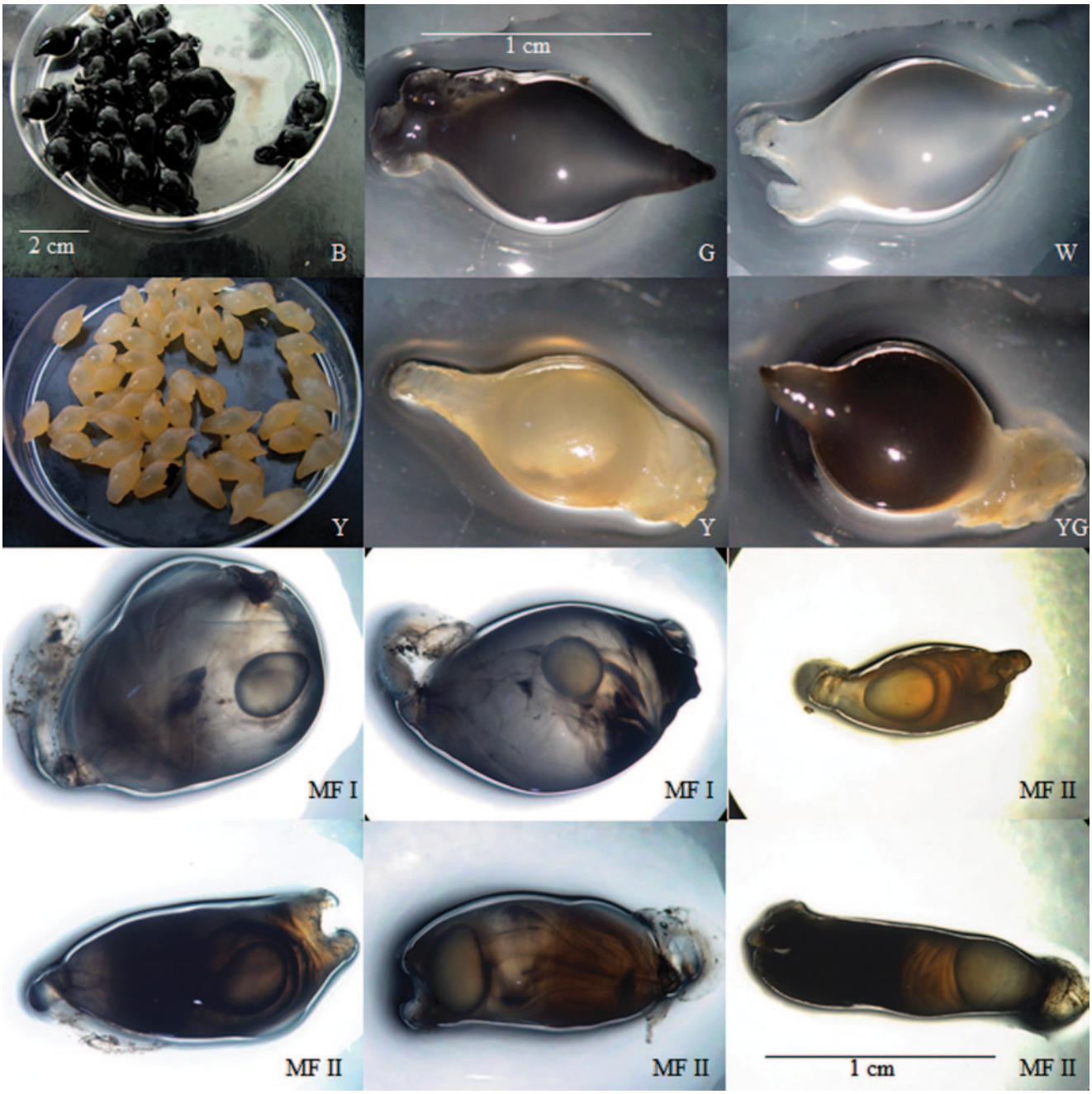

Fig. 11.3 Below ground metal pools among the different nitrogen fertilization treatments (average ± standard deviation)

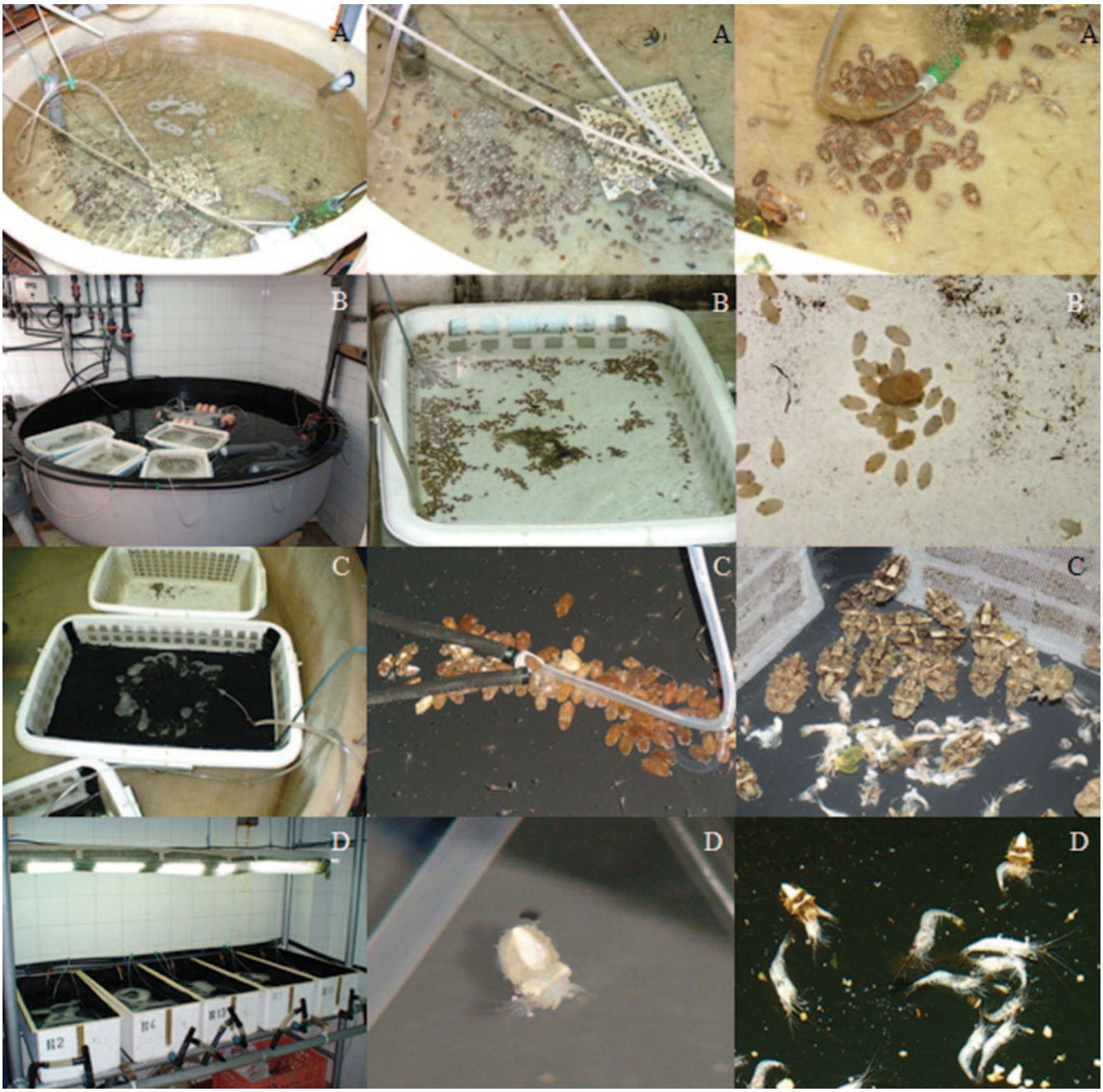

Fig. 11.4 Above ground metal pools among the different nitrogen fertilization treatments (average ± standard deviation)

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Household Detergents Causing Eutrophication in Freshwater Ecosystems

12

Abid A. Ansari and Fareed A. Khan

Abstract

In the present study, the impact of some selected household detergents has been studied on the growth behavior and development of two freshwater duckweeds, namely *Lemna minor* and *Spirodela polyrrhiza*. The growth responses of these selected free-floating duckweeds to varying concentrations of "Surf Excel" (the most commonly used detergent) have been studied with special reference to varying temperature and pH. There were three predominant types of growth pattern of both the selected duckweeds treated with 36 selected detergents. Some of the detergents increased the growth of the two duckweeds in almost logarithmic progression showing increase in growth with increasing concentration (10–50 ppm). A few detergents increased growth of both the selected duckweeds to a certain level of detergent concentration and then the growth became stationary with further increase in detergent concentration. In the third type of response, the duckweed growth initially increased in response to a certain level of detergent concentration and declined at higher detergent concentration. It was inferred from the observations that detergents play important role in promoting the growth of duckweeds. Out of 36 detergents studied, certain detergents effectively promoted the growth of duckweeds even in low concentration. Certain brands of detergents resulted in consistent increase in the growth with increasing concentration. The temperature effectively modified the duckweed response to the detergent. The cooler water medium had lesser degree of eutrophication than the moderately warm water medium. Not the phosphorus content alone, but the water quality (turbidity, pH, nutrient concentration, and dissolved oxygen) modified by the detergent aggravated the problem of eutrophication. Therefore, the water bodies receiving acids from any source in addition to detergent are more likely to show a greater degree of eutrophication than a body receiving detergent without acids.

Keywords

Eutrophication · *Lemna minor* · *Spirodela polyrrhiza* · Detergents

12.1 Introduction

The water is an essential life supporting matter in every cell of an organism. It enters into the living organisms via absorption or ingestion. It circulates between biotic and abiotic components of the ecosystem. The misuse and reckless over consumption has resulted into the fast depletion of water resources (Ansari and Khan 2007). The nutrient enrichment of the water bodies caused from the natural and man-made

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sources is depleting the water resources at a faster pace. The eutrophication is a kind of nutrient enrichment process of any aquatic body which results into an excessive growth of phytoplankton (Ansari and Khan 2006a). The phosphate rocks and mineral sedimentation are the natural sources of phosphorus into the terrestrial and aquatic ecosystems. The household detergents containing phosphates and phosphorus fertilizers used in the agricultural practices are the major anthropogenic sources of phosphorus (Ansari 2005).

Eutrophication is one of the serious kinds of water pollution directly affecting the fauna owing to the loss of dissolved oxygen level. It leads to an early and relatively faster mortality rate of fishes and thus spoils the desired water qualities of ponds or lakes. The fishing operation and navigation becomes difficult owing to enmeshed and heavy growth of plants. The hydroelectric generation from such water storages is adversely affected as nutrient-rich water (of such reservoirs) acts chemically upon the turbines (Khan and Ansari 2005). At the end of algal bloom, the decomposing debris also spoils the desired water characteristics and may bring in the growth of disease-causing bacteria. An uncontrolled eutrophication leads to a rapid upwelling of a water body (Ansari and Khan 2009a, b). The limited storage and water recharging capacity of smaller freshwater bodies reduces by silting. Small lakes and many ponds steadily lose their aquatic entity and become permanently terrestrial in nature (Ansari et al. 2011a, b).

The common household detergents are the major anthropogenic source of phosphorus input into the nearby water bodies and sewage treatment plants. The detergents normally consist of two basic components the surfactants and the builders. The surfactants also called surface-active agents are the main cleaning agents. We can find various brands of detergents in the markets containing 10–30% surfactants (Rao 1998; Khitoliya 2004). The remaining parts of detergents are the builders as polyphosphate salts. About 1 ppm of surfactant produces a huge amount of foam in water bodies. This concentration is non-toxic to human being but gives an off-taste to drinking water and exerts a significant impact on ecosystem. Just 0.1 ppm of surfactant can reduce the rate of oxygen absorption in water to about half (Rao 1998).

Chemically the surfactants are linear alkyl sulphonate. At present, the release of polyphosphate builders into natural water is great environmental problem than the surfactants. It causes eutrophication of the water bodies in which it is released. Nitrilotriacetate was considered to be a replacement of polyphosphate builder but it proved to be hazardous to human health. The best alternative is to minimize the use of phosphates in detergents (Rao1998).

The members of the duckweeds family Lemnaceae are small free-floating plants which propagate rapidly. They are very sensitive to many factors of surrounding environment (Lau and Lane 2002a, b). Their potentials to use as indicators of water quality have been studied by several workers (Ansari and Khan 2011c; Srivastava and Jaiswal 1989). Duckweeds are appropriate material for the investigation of metal accumulation and its toxicity. The duckweeds change their morphology growth rate in response to even a very small amount of water pollutant (Ansari and Khan 2008; Jaiswal and Srivastava 1987). On certain criteria Thornton et al. (1986) considered *Lemna minor* as ecologically sensitive species. The growth of *Spirodela polyrrhiza* was found directly related with the type and nature of the water (Ansari and Khan 2002). Duckweed species are promising macrophytes for the use in sustainable wastewater treatment owing to their rapid growth, ease of harvest and feed potential as a protein source. The duckweeds showed a high growth rate and productivity in well-managed system (Ansari and Khan 2009b, 2011d; Edwards 1985, 1992). The duckweeds have been found responsible for three-quarters of the total nitrogen (N) and phosphorus (P) loss in very shallow aquatic systems (Korner et al. 2003) and thus have potentials of phytoremediation. The duckweed growth shows a direct response to the chemical composition of water (Landolt 1986). Wastewater concentrations and seasonal climate conditions had direct impacts on duckweed growth and nutrient uptake by these plants (Cheng et al. 2002).

In the present work experiments were designed to study the extent of eutrophication caused by 36 selected household detergents in the fresh water ecosystem. The growth behavior of the selected duckweeds namely *Lemna minor* (L.) and *Spirodela polyrrhiza* (L.) of family Lemnaceae was studied as a measure of eutrophication caused by detergents. In the present work, growth behavior of both the free-floating duckweeds have been studied with special reference to "Surf Excel" detergent powder commonly used in India.

12.2 Materials and Methods

12.2.1 Selection and Collection of Plant Material

The two common duckweeds namely *Lemna minor* (L.) and *Spirodela polyrrhiza* (L.) Shield of family Lemnaceae were selected for the experiments. The individuals of both the species were collected with the help of tea strainer from the fresh water bodies of civil line area of Aligarh. Both the selected duckweeds were brought to the laboratory in separate polyvinyl containers with adequate quantity of water. The collected duckweeds were washed 3–4 times with tap water.

12.2.2 Botanical Description of Selected Plants (Pandey 1997)

12.2.2.1 *Lemna minor* (L.)

Habit They are the smallest and least differentiated angiosperms of the world. They are aquatic in nature and found floating in fresh waters.

Diversity and distribution The species of *Lemna* are widely distributed in both temperate and tropical parts of the globe except in arctic regions.

Plant morphology The plant body consists of green dorsiventral scale like shoots. The shoots of *Lemna* range from 1/8 to 3/4 in. The plants do not possess leaves and flat green shoot perform the functions of leaf. The plant body may easily be differentiated into a basal portion with two lateral pockets from which the branches arise. From the ventral surface of the flattened stem a single adventitious root come out. The apex of root is converted by a few layered sheaths (root cap) which is visible to the unaided eyes.

The internal structure of the shoot is spongy in nature and consists of parenchymatous cells. These cells remain separated from each other by large or small air spaces, which communicate with the outside by stomata on the upper surface. Vascular tissue is represented by a single median vascular bundle of very simple structure.

Inflorescence In temperate zones, the flowers are rarely developed. The inflorescence is quite simple and arises in the pocket.

Flowers The flowers are unisexual. The plants are monoecious, i.e., both male and female flowers develop in the same inflorescence. The flowers are without perianth (naked). The male flower consists of single stamen. The filament is stout bearing at its apex a pair of dithicous anther-halves. The pollen grains are spherical and covered with small warty outgrowths. The female flower consists of single carpel. The pistil is flask shaped with a short funnel-shaped stigma. The ovary is unilocular with one to six basal, erect, orthotropous, or more or less completely anatropous ovules.

Fruit Inconspicuous, usually one seeded.

Seed The seed possess a thick fleshy outer and a thin inner coat. The embryo consists of a large cotyledon surrounded by scanty endosperm.

Pollination The pollination is affected by wind, water, or animals.

Propagation New plant buds arise from the pockets on either side of the parent plant and eventually break apart. Over winters as winter buds on the lake bottom, but rarely reproduces from seeds. A plant can reproduce itself about every 3rd day under ideal conditions in nutrient rich waters.

Importance of plant Food for fish and waterfowl and habitat for aquatic invertebrates. Because of its high nutritive value, duckweeds have been used for cattle and pig feed in Africa, India, and southwest Asia. They are also used to remove nutrients from sewage effluents.

12.2.2.2 *Spirodela polyrrhiza* (L.) Shield

Habit They are the smallest and least differentiated angiosperms of the world. They are aquatic in nature and found floating in fresh waters.

Diversity and distribution The species of *Spirodela* are widely distributed in both temperate and tropical parts of the globe except in arctic regions.

Plant morphology The plant body consists of green dorsiventral scale-like shoots. There are no leaves and flat green shoot perform the functions of leaf. The plant body (thallus) is actually an expended "stem" which functions as leaf. It is oval to oblong, has 5–12 distinct veins and is 4–10-mm long. The thallus is glossy green and smooth on the upper surface and reddish purple below. Clusters of 4–16 slender fibrous roots hang below the surface of the water from each plant. Each roots ends with a pointed root cap.

The internal structure of the shoot is spongy in nature and consists of parenchymatous cells. These cells remain separated from each other by large or small air spaces, which communicate with the outside by stomata on the upper surface. Vascular tissue is represented by a single median vascular bundle of very simple structure.

Inflorescence In temperate zones, the flowers are rarely developed. The inflorescence is quite simple and arises in the pocket.

Flowers The flowers are unisexual. The plants are monoecious, i.e., both male and female flowers develop in the same inflorescence. The flowers are without perianth (naked). The male flower consists of single stamen. The filament is stout bearing at its apex a pair of dithicous anther-halves. The pollen grains are spherical and covered with small warty outgrowths. The female flower consists of single carpel. The pistil is flask shaped with a short funnel-shaped stigma. The ovary is unilocular with one to six basal, erect, orthotropous, or more or less completely anatropous ovules.

Fruit A ribbed seed develops in a balloon like bag (utricle).

Seed The seed possess a thick fleshy outer and a thin inner coat. The embryo consists of a large cotyledon surrounded by scanty endosperm.

Pollination The pollination is affected by wind, water or animals.

Propagation Reproduces quickly by asexual budding, seeds and over winters as dark green or buds on the sediments.

Importance of plant Provides a high protein food source for ducks and geese, also eaten by certain fish in Africa and Asia, giant duckweed has been harvested for cattle and pig feed. Grows quickly, especially the water is warm and nutrient enriched. It has been used to reduce nutrients in sewage effluents.

12.2.2.3 Classification of *Lemna minor* and *Spirodela polyrrhiza* (Pandey 1997)

12.2.3 Culture and Stock of the Selected Duckweeds

Bentham and Hooker (1862)	Engler and Prantl (1931)	Hutchinson (1959)
Phanerogams	Phanerogams	Angiospermeae
Monocotyledones	Monocotyledoneae	Monocotyledones
Nudiflorae	Spathiflorae	Corolliferae
Lemnaceae	Lemnaceae	Arales
–	–	Lemnaceae

The plants of *Lemna minor* (L.) and *Spirodela polyrrhiza* (L.) grow vegetatively and quickly. The duckweeds collected were cultured in larger bowl-shaped earthen pots locally called as *Nand*. The approximate size of these pots was 40-cm diameter, 25-cm depth and 19 L capacity. The pots were filled with 15 L of tap water. After a lag phase of 24 h, 15 mL macronutrient (Hoagland) solution (Mahadevan and Sridhar 1986), 1 mL of water was added in culture pots (Table 12.1). The total volume of 15 L of water in the earthen pot was maintained every 24 h by maintaining the marked water level. The pure stock/culture of single duckweed was separately maintained by constant removing of any other weed appearing in the pure culture.

Table 12.1 Stock solution of macronutrients (Hoagland solution)

Macronutrients	g/L
$NH_4H_2PO_4$	0.23
KNO_3	1.02
$Ca(NO_3)$	0.492
$MgSO_47H_2O$	0.49

12.2.4 Setting of Experimental Pots

The required individuals of *Lemna minor* and *Spirodela polyrrhiza* (of approximately mature body size) were carefully transferred from the maintained duckweed stocks to the experimental pots (filled with detergent solution of varying concentration and Trade brands) with the help of small painting brush (No. 2).

12.2.5 Treatments and Detergent Solution

In the screening experiment the selected duckweeds were treated with three concentrations of commonly available detergents under 36 brand names (Table 12.2). In the screening experiments 10 ppm, 30 ppm, and 50 ppm of each detergent were prepared in tap water and used as T_1, T_2, and T_3. A control as T_0 having no detergent but the tap water was also maintained for the reference (Tables 12.3, 12.4). In rest of the experiments, the growth performances of the selected duckweeds were studied in five varying concentrations of a selected detergent "Surf Excel" and a control (tap water).

The treatment named as T_0 consisted of simple tap water (without detergent). The treatments T_1, T_2, T_3, T_4, and T_5 consisted of 10, 20, 30, 40, and 50 ppm of "Surf Excel" in tap water, respectively (Tables 12.3 and 12.4). The required detergent solutions were prepared from the 100 mL stock solutions of 1, 2, 3, 4, and 5 % of detergent cakes or powders in tap water by further dilutions. Owing to hygroscopic nature, the detergent cakes and powders used in the present experiments were oven dried at 60 ° for 24 h before weighing.

12.2.6 Experiments Designed

The first two experiments were designed to work out the growth response (in terms of dry weight) of the selected duckweeds to varying concentrations of the 36 selected detergents dissolved in the tap water (Tables 12.2, 12.3 and 12.4). The first screening experiment was conducted on *Lemna minor* and second on *Spirodela polyrrhiza*. In the screening experiment with *Lemnaminor* and *Spirodela polyrrhiza,* 1 g of each plant of almost equal size were transferred from the maintained pool to polyvinyl pots of containing 500 mL of the detergent solution (of a desired concentration). The pots of each detergent and their concentration were maintained in

Table 12.2 List of the detergent products used in screening experiments

S. No.	Brand Name	Form	Product by
1	Ariel	Cake	Procter and Gamble Home Products Ltd. Mumbai
2	Ariel	Powder	Procter and Gamble Home Products Ltd. Mumbai
3	Budget	Cake	Kothari detergent Ltd. Kanpur
4	Doctor	Cake	P.C.Cosma Soap Pvt. Ltd. New Delhi
5	Doctor	Powder	P.C.Cosma Soap Pvt. Ltd. New Delhi
6	Double Dog	Powder	KTC Pvt. Ltd. Kanpur
7	Cleano	Powder	Garud Homo-Cleanse Pvt. Ltd. Delhi
8	Fena	Cake	Fena Pvt. Ltd. New Delhi
9	Fena	Powder	Fena Pvt. Ltd. New Delhi
10	Friendly Wash	Powder	Henkel Spic India Ltd. Chennai
11	555	Cake	GoramalHariram Ltd. New Delhi
12	Ghari	Cake	KTC Pvt. Ltd. Kanpur
13	Ghari	Powder	KTC Pvt. Ltd. Kanpur
14	Henko	Cake	Henkel Spic India Ltd. Chennai
15	Henko	Powder	Henkel Spic India Ltd. Chennai
16	Maxclean	Powder	Wiseman Home Products
17	Mor	Cake	Sagar Detergent Pvt. Ltd. Kanpur
18	Mor	Powder	Sagar Detergent Pvt. Ltd. Kanpur
19	Morlight	Powder	Sagar Detergent Pvt. Ltd. Kanpur
20	Mr. White	Powder	Henkel Spic India Ltd. Channai
21	Nirma	Cake	Nirma Ltd. Ahmadabad
22	Nirma	Powder	Nirma Ltd. Ahmadabad
23	Nirma Super	Powder	Nirma Ltd. Ahmadabad
24	Plus	Cake	Corona Plus Inds. Ltd. Mumbai
25	Plus	Powder	Corona Plus Inds. Ltd. Mumbai
26	Plus (Extra)	Powder	Corona Plus Inds. Ltd. Mumbai
27	Plus (Saving)	Powder	Corona Plus Inds. Ltd. Mumbai
28	Rin	Cake	Hindustan Lever Ltd. Mumbai
29	Rin Shakti	Powder	Hindustan Lever Ltd. Mumbai
30	Rin Supreme	Powder	Hindustan Lever Ltd. Mumbai
31	Surf	Powder	Hindustan Lever Ltd. Mumbai
32	Surf Excel	Powder	Hindustan Lever Ltd. Mumbai
33	Tide	Powder	Procter and Gamble Home Products Ltd. Mumbai
34	Time-Zee	Powder	Ramnagar Khadi Gram udyog Samiti. Chandauli
35	Wheel	Cake	Hindustan Lever Ltd. Mumbai
36	Wheel	Powder	Hindustan Lever Ltd. Mumbai

triplicates. The duckweeds were allowed to grow for another 10 days. The day of transfer of plants was counted as day-1. The experiments were terminated on 11th day and plants were harvested, dried in oven at 80 °C for 24 h and weighed (as per the scheme given in Table 12.4).

The detailed studies on the responses of the two selected weeds to 0, 10, 20, 30, 40, and 50 ppm of Surf Excel were carried out in large earthen pots (locally called as *Nand*) filled with 15 L of the detergent solution (Table 12.4). In these pots 5 g of *Lemna minor* and *Spirodela polyrrhiza* were inoculated in separate experiments on day 1st from the pure duckweed stocks. Growth of *Lemna minor* and *Spirodela polyrrhiza* was recorded at 11th day of transplant in the pots. The uptake of NPK, chlorophyll content (*a*, *b*, and total), dry weight and physico–chemical properties of detergent solutions were also determined after the termination of experiments on 11th day (Table 12.4).

Table 12.3 Scheme of treatments of the selected duckweeds with varying concentrations of detergent in various experiments conducted in polyvinyl and earthen pots.

Treatments (each in triplicate)	Screening experiment with the listed 36 detergents	Experiment with Surf Excel
T_0 (control)	0 ppm (tap water only)	0 ppm (tap water only)
T_1	10 ppm	10 ppm
T_2	30 ppm	20 ppm
T_3	50 ppm	30 ppm
T_4	–	40 ppm
T_5	–	50 ppm

Two separate experiments were conducted in polyvinyl pots to evaluate the effect of temperature variation (viz.10, 20, 30, 40 and 50 °C) and its interaction with varying concentrations of Surf Excel detergent on growth responses of duckweeds. The polyvinyl pots inoculated with 1 g of *Lemna minor* or *Spirodela polyrrhiza* were placed in BOD incubator (Caltan, Narang Scientific Works Pvt. Ltd., New Delhi) for the temperature treatments maintained at 10, 20, 30, 40, or 50 °C. The growth in all pots was recorded after the termination of the experiments (Table 12.4). Owing to early mortality of *Lemna minor* at higher temperatures 40 and 50 °C, the growth parameters were recorded finally at 7th and 5th day, respectively. These parameters of *Spirodela polyrrhiza* maintained at 40 and 50 °C temperature were finally recorded at 9th and 5th day, respectively. The plants with maximum brownish or yellowish appearance (chlorosis) were treated as dead.

Two experiments were conducted to study the effect of pH variation on the responses of selected duckweeds to varying levels of Surf Excel detergent in the ecosystem at a given temperature. The pH of detergent solutions and tap water was maintained at pH 6.0, 6.5, 7.0, 7.5, and 8.0 by using NaOH or HCl. The data on growth parameters were recorded as in previous experiments (Table 12.4).

12.2.7 Data Recording

The data on growth of both the selected species in all sets of experiments were recorded at 11th day stage. The water and plant analysis was also carried out after the termination of experiments (on 11th day or earlier as in experiments with temperature treatments). The data so obtained were analyzed

Table 12.4 A summary of the designed experiments

Species and individuals inoculated at day-1	Treatments (detergent in tap water)	Pot type, Volume and replicates	Parameters studied
Lemna minor, 1 g individuals in each **polyvinyl pot**	0 (control), 10, 30 and 50 ppm of the 36 selected detergents (solution 500 ml)	Polyvinyl pots, 500 mL, 3 replicates	Dry weight after termination, at 11th day
Spirodela polyrrhiza, 1 g individuals in each **polyvinyl pot**	0 (control), 10, 30 and 50 ppm of the 36 selected detergents (solution 500 ml)	Polyvinyl pots, 500 mL, 3 replicates	Dry weight after termination, at 11th day
Lemna minor, 5 g individuals in each *earthen pot*	0 (control), 10, 20, 30, 40 and 50 ppm of Surf Excel detergent powder (solution 15 L)	Earthen pots, 15 L (Nand), 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis
Spirodela polyrrhiza, 5 g individuals in each **earthen pot**	0 (control), 10, 20, 30, 40 and 50 ppm of Surf Excel detergent powder (solution 15 L)	Earthen pots, 15 L (Nand), 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis
Lemna minor, 1 g individuals in each **polyvinyl pot**	Temperature variations, 10, 20, 30, 40 and 50 °C at each treatment level (0, 10, 20, 30, 40 and 50 ppm) of Surf Excel, pH constant = 7.0	Polyvinyl pots, 500 mL, 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis[a]
Spirodela polyrrhiza, 1 g individuals in each **polyvinyl pot**	Temperature variations,10, 20, 30, 40 and 50 °C at each treatment level (0, 10, 20, 30, 40 and 50 ppm) of Surf Excel, pH constant = 7.0	Polyvinyl pots, 500 mL, 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis[b]
Lemna minor, 1 g individualsin each **polyvinyl pot**	pH variations, 6.0, 6.5, 7.0, 7.5 and 8.0 at each treatment level (0, 10, 20, 30, 40 and 50 ppm) of Surf Excel, temperature constant = 30 °C	Polyvinyl pots, 500 mL, 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis
Spirodela polyrrhiza, 1 g individuals in each **polyvinyl pot**	pH variations, 6.0, 6.5, 7.0, 7.5 and 8.0 at each treatment level (0, 10, 20, 30, 40 and 50 ppm) of Surf Excel, temperature constant = 30 °C	Polyvinyl pots, 500 mL, 3 replicates	Growth parameters and uptake of NPK at 11th day, water analysis

[a] The *Lemna minor* showed an early maturity and death (complete chlorosis) at 40 and 50 °C. The growth parameters and uptake of NPK at 40 and 50 °C were recorded at 7th and 5th day, respectively after the death of the plants
[b] The *Spirodela polyrrhiza* showed an early maturity and death (complete chlorosis) at 40 and 50 °C. The growth parameters and uptake of NPK at 40 and 50 °C were recorded at 9th and 5th day, respectively after the death of the plants

statistically following Dospekhov (1984) for mean ± standard deviation, percent variation, and significance of the variation over control.

12.2.8 Parameters Studied

The following parameters were studied:

12.2.8.1 Characteristics of the Varying Concentrations of Detergent Solution

1. Turbidity
2. pH
3. Dissolved oxygen
4. Nitrates
5. Phosphates
6. Potassium

12.2.8.2 Growth Parameters

1. Dry weight of plant
2. Chlorophyll *a*
3. Chlorophyll *b*
4. Total chlorophyll

12.2.8.3 Nutrient Uptake in Plants

1. Nitrogen content
2. Phosphorus content
3. Potassium content

Characteristics of Varying Grades of Detergent Solutions

The water analysis of varying grades of detergent solution was carried out following Trivedi et al. (1987). The turbidity, pH, dissolved oxygen, nitrates, phosphates, and potassium contents of detergent solution were analyzed after the termination of experiments.

1. pH

The pH was determined with the help of pH meter (Elico, Elico Ltd. Hyderabad, India). The pH meter was calibrated with standard buffer of known pH before use.

2. Turbidity

Turbidity was determined with the help of Nephroturbidity meter (Elico, Elico Ltd. Hyderabad, India). The turbidity meter was calibrated with the standard solutions of known turbidity.

3. Dissolved oxygen (DO)

Dissolved oxygen content was calculated with the help of following formula:

$$DO = \frac{(ml \times N) \text{ of sodium thiosulphate} \times 8 \times 1000}{V_2[(V_1 - V)/V_1]} mg/1$$

Where, V_1 = volume of sample bottle
V_2 = volume of content titrated
V = volume of $MnSO_4$ and KI added (2 mL) to the sample

4. Nitrates
Nitrates were calculated from the standard pattern. Standard pattern was prepared between concentration of nitrates and absorbance from 0.0 to 1.0 mg/L of nitrates at the NO_3-N at the interval of 0.1 by finding the absorbance of standards.
5. Phosphates
The concentration of phosphate calculated with help of standard pattern. The standard pattern was prepared in the range of 0.0 to1.0 mg/L of PO_4-P at the interval of 0.1, following the same method described for the NO_4-N.
6. Potassium
The estimation of potassium was carried out directly with the help of flame photometer (AIMIL, Aimil Sales and Agencies Pvt. Ltd., New Delhi) using appropriate filter and a standard pattern by taking known concentration of potassium.

Growth Parameters
1. Dry weight of plant
Plants dried at 80 °C for 24 h after the termination of experiment and dry weight was taken per gram of fresh material.
2. Chlorophyll estimation
The optical density of chlorophyll solution read at 645 nm and 663 nm wave lengths with the help of Spectronic-20 Spectrophotometer (Elico, Elico Ltd. Hyderabad, India). The chlorophyll contents were calculated according to the formula given by Arnon (1951) as given below:

$$\text{Chlorophyll } a\,(\text{mg/g of fresh tissue}) = \frac{12.7\,(\text{O.D.}663) - 2.69\,(\text{O.D.}645) \times \text{V}}{1000 \times \text{W}}$$

$$\text{Chlorophyll } b\,(\text{mg/g of fresh tissue}) = \frac{22.9\,(\text{O.D.}645) - 4.68\,(\text{O.D.}663) \times \text{V}}{1000 \times \text{W}}$$

$$\text{Total Chlorophyll}\,(\text{mg/g of fresh tissue}) = \frac{20.2\,(\text{O.D.}645) + 8.02\,(\text{O.D.}663) \times \text{V}}{1000 \times \text{W}}$$

Where, O.D. = optical density (absorbance) at given wave lengths viz. 645 and 663 nm.
V = total volume of chlorophyll extract prepared in 80 % acetone.
W = fresh weight of plant tissue in g.

Nutrient Uptake
To determine the nutrient uptake of plant the samples were digested according to Lindner (1944) for the estimation of N, P, and K.
1. Estimation of nitrogen
The nitrogen was estimated following the method of Lindner (1944). The solution of standard pattern and samples were read for their absorbance at 525 nm using Spectronic-20 Spectrophotometer. A calibration pattern was plotted with optical density on X-axis and known concentration of ammonium sulfate on Y-axis, nitrogen was expressed in terms of percentage on dry matter bases.
2. Estimation of phosphorus
Phosphorus contents in digested material were estimated by the method of Fiske and Subbarow (1925). Optical density of the solution (sample) was read at 625 nm using Spectronics-20 Spectrophotometer. A standard pattern was prepared using different dilutions of KH_2PO_4 solution versus optical density. With the help of standard pattern the content of phosphorus in terms of percentage on dry matter base was determined.
3. Estimation of potassium
The potassium contents were estimated by Flamephotometer (Elico, Elico Ltd. Hyderabad, India). The readings were compared with the help of calibration pattern plotted with the help of known dilutions of KCl solution. The potassium was expressed in terms of percentage on a dry weight bases.

12.3 Observations

In the present work, impact of 12 detergent cakes and 24 detergent powders commonly sold in the Indian market on the growth (in terms of dry weight) of selected duckweeds namely *Lemna minor* and *Spirodela polyrrhiza* have been studied. The growth responses of the selected duckweeds maintained in small plastic pots containing varying concentrations of all the selected detergents are given below. In both the weeds three general types of pattern of absolute growth were observed (as given).

12.3.1 Growth Pattern

There were three general types of absolute growth pattern as **type-A**, **type-B**, and **type-C** observed in the duckweed growth treated with 36 selected detergents. Type-A pattern shows a consistent increase in growth of the duckweed with increasing concentration of some detergents. The peak of growth was recorded at 50 ppm level of detergent. Type-B growth pattern shows an increase in growth up to 30 ppm and then a decline at higher concentration. In type-C growth pattern there was an increase in the duckweed growth at lower dose (10 ppm) of detergents and then it decreased with further detergent concentration. Type-A pattern of growth resemble with the growth pattern of algal bloom in a medium with unlimited environment (Kormondy 1994). The growth pattern type-A is closer to positive linear line between the growth and detergent concentration. The *Lemna minor* and *Spirodela polyrrhiza* treated with a large number of detergent cakes showed predominantly growth pattern type-A

Table 12.5 Dry weight (mg g^{-1} of fresh weight) of *Lemna minor* treated in small plastic pots with varying doses of 12 selected detergent cakes

Detergent (Brand name)	Control	Concentration (ppm)			LSD at	
	0	10	30	50	5%	1%
Ariel	113.54 ± 1.04	114.62 ± 1.0 (+0.95%)	118.67 ± 1.37 (+4.52%)	116.27 ± 1.40 (+2.40%)	0.86	1.30
Budget	113.54 ± 1.04	114.98 ± 1.90 (+1.27%)	116.49 ± 1.72 (+2.60%)	115.46 ± 1.20 (+1.69%)	1.60	2.43
Doctor	113.54 ± 1.04	115.69 ± 1.06 (+1.89%)	117.75 ± 1.53 (+3.71%)	116.08 ± 1.2 (+2.24%)	0.58	0.88
Fena	113.54 ± 1.04	117.79 ± 1.72 (+3.74%)	113.69 ± 0.62 (+0.13%)	114.33 ± 1.31 (0.70%)	2.51	3.81
555	113.54 ± 1.04	114.90 ± 1.05 (+1.20%)	115.52 ± 1.45 (+1.74%)	113.84 ± 1.46 (+0.26%)	NS	NS
Ghari	113.54 ± 1.04	115.31 ± 1.54 (+1.56%)	115.21 ± 1.26 (+1.47%)	114.75 ± 0.96 (+1.07%)	0.66	1.00
Henko	113.54 ± 1.04	113.89 ± 1.10 (+0.31%)	119.77 ± 1.57 (+5.49%)	115.44 ± 0.91 (+1.67%)	0.71	1.08
Mor	113.54 ± 1.04	115.01 ± 1.08 (+1.29%)	115.87 ± 0.73 (+2.05%)	114.51 ± 1.33 (+0.85%)	NS	NS
Nirma	113.54 ± 1.04	116.12 ± 1.13 (+2.27%)	120.43 ± 1.22 (+6.07%)	115.40 ± 0.73 (+1.64%)	0.53	0.80
Plus	113.54 ± 1.04	116.56 ± 0.60 (+2.66%)	115.37 ± 1.31 (+1.61%)	113.96 ± 1.27 (+0.37%)	0.81	1.22
Rin	113.54 ± 1.04	115.68 ± 1.57 (+6.52%)	120.94 ± 1.06 (+1.88%)	115.21 ± 1.32 (+1.47%)	0.71	1.08
Wheel	113.54 ± 1.04	114.80 ± 0.96 (+1.11%)	122.19 ± 1.10 (+7.62%)	117.09 ± 1.04 (+3.12%)	0.15	0.23

Mean ± SD, within parenthesis-per cent variation over the control

followed by type-B. Only fewer detergent cakes showed type-C response.

The *Lemna minor* treated with detergent powders showed predominantly type-B and type-C pattern followed by type-A growth response as observed on treatment with only seven detergent powders. Treatment of *Spirodela polyrrhiza* with most of the detergent powders showed predominantly type-A and B pattern. It is inferred from the growth pattern that most of the detergents whether in the form of cake or powder promoted the growth exponentially without any toxic effect up to 50 ppm concentration. Only few detergents showed toxicity to these two weeds at high concentration of 50 ppm.

12.3.2 Impact of Some Selected Detergents on Dry Weight of *Lemna minor*

Table 12.5 comprises the data on dry weight of *Lemna minor* treated in small plastic pots with varying concentrations of 12 common detergents sold in the form of cakes. Dry weight per gram of fresh plant (*Lemna minor*) significantly increased on treatments with 10 and 30 ppm of detergent as compared to the control (0 ppm). The dry weight accumulation was relatively lower at 50 ppm of all the 12 selected detergent cakes. The impact of treatment with Ariel detergent on dry weight of *Lemna minor* increased with concentration up to 30 ppm. The 30 ppm of Henko, Nirma, Rin, and Wheel detergent cakes also significantly enhance the dry weight of *Lemna minor*. The accumulation of dry weight was relatively lower in *Lemna* species treated with 50 ppm of these detergents. The impact of Budget, Doctor, Fena, 555, Ghari, Mor, and Plus detergent cakes was far lesser in comparison to the other detergents cakes studied (Table 12.5).

Table 12.6 summarizes the data on dry weight accumulation of *Lemna minor* treated with three varying doses of 24 selected detergent powders. The impact of detergent powders on dry weight of *Lemna minor* was relatively higher than the detergent cakes. Among few common brands of detergents like Ariel, Double Dog, Fena, Friendly Wash, Ghari, Henko, Mr. White, Nirma, Rin Supreme, Surf, Surf Excel, Tide, and Wheel, the impact of Surf and its new brand Surf Excel on the dry weight of *Lemna minor* was relatively higher than the other detergent powders under study. The dry weight accumulation significantly increased in *Lemna minor* on treatment with 30 ppm of Surf and its new brand Surf Excel. The other detergents like Doctor, Mor, Nirma Super, Plus and its new brand Extra Plus, and Rin Shakti had a relatively lesser degree of impact on the dry weight of *Lemna minor*. The impact of varying concentrations of less popular detergents like Cleano, Morlight, Saving Plus, and Time-Zee on the dry weight of *Lemna minor* was statistically nonsignificant (Table 12.6).

12.3.3 Impact of Some Selected Detergents on Dry Weight *Spirodela polyrrhiza*

The data on dry weight of *Spirodela polyrrhiza* treated in small plastic pots with varying concentrations of 12 selected detergent cakes are summarized in Table 12.7. There was a significant increase in the dry weight of *Spirodela polyrrhiza* on treatment with Ariel detergent cake. The dry weight of plants was significantly increased with the increase in concentration up to 30 ppm. There was relatively higher dry weight accumulation in *Spirodela polyrrhiza* treated with varying concentrations of 555, Henko, Nirma, Rin, and Wheel detergent cakes. The impact of all concentrations of Doctor, Fena, Ghari, and Mor detergent cakes on dry weight of *Spirodela polyrrhiza* was lesser than the impact of other detergents studied. Statistically there was no significant change in the dry weight of *Spirodela polyrrhiza* treated with varying concentrations of Budget and Plus detergent cakes. The high concentration (50 ppm) of Henko, Nirma, and Rin enhanced the dry weight accumulation to a noticeable extent (Table 12.7).

Table 12.6 Dry weight (mg g^{-1} of fresh weight) of *Lemna minor* treated in small plastic pots with varying doses of some common detergent powders

Detergent (Brand name)	Control	Concentration (ppm)			LSD at	
	0	10	30	50	5%	1%
Ariel	113.35±1.40	118.32±1.49 (+4.74%)	123.80±1.03 (+9.22%)	118.34±1.22 (+4.40%)	0.50	0.76
Cleano	113.35±1.40	114.20±1.34 (+0.75%)	114.71±1.11 (+1.20%)	115.45±1.31 (+1.85%)	NS	NS
Doctor	113.35±1.40	114.36±1.33 (+0.89%)	115.29±1.10 (+1.72%)	116.22±1.30 (+2.54%)	0.31	0.47
Double Dog	113.35±1.40	122.26±1.25 (+7.86%)	116.50±1.12 (+2.78%)	117.22±1.13 (+3.41%)	0.32	0.48
Fena	113.35±1.40	116.35±1.41 (+2.65%)	119.45±0.91 (+5.38%)	116.13±1.05 (+2.45%)	0.62	0.94
Friendly wash	113.35±1.40	119.50±0.87 (+5.43%)	114.75±1.16 (+1.24%)	125.31±1.66 (+10.55%)	0.84	1.27
Ghari	113.35±1.40	113.40±1.44 (+0.04%)	119.82±1.40 (+5.71%)	114.95±1.36 (+1.41%)	1.15	1.74
Henko	113.35±1.40	116.75±1.17 (+2.30%)	122.75±1.79 (+8.29%)	118.96±1.26 (+4.95%)	0.67	1.02
Max Clean	113.35±1.40	113.87±1.17 (+0.46%)	116.23±1.21 (+2.54%)	116.71±0.94 (+2.96%)	0.46	0.70
Mor	113.35±1.40	114.52±1.36 (+1.03%)	117.44±1.87 (+3.61%)	116.83±1.11 (+3.07%)	0.33	0.50
Mor light	113.35±1.40	113.47±1.40 (−0.2%)	115.01±1.09 (+1.47%)	114.71±1.13 (+1.20%)	NS	NS
Mr. white	113.35±1.40	121.73±1.04 (+7.39%)	117.35±0.93 (+3.53%)	115.10±1.12 (+1.54%)	0.49	0.74
Nirma	113.35±1.40	115.22±0.42 (+1.65%)	120.82±1.17 (+6.59%)	115.00±1.91 (+1.46%)	1.03	1.56
Nirma (Super) [a](Super Nirma)	113.35±1.40	120.52±0.73 (+6.33%)	113.87±0.90 (+0.46%)	115.03±0.99 (+1.48%)	0.69	1.04
Plus	113.35±1.40	116.73±1.08 (+2.98%)	115.58±0.98 (+1.97%)	113.49±1.28 (+0.12%)	0.46	0.70
Plus (Extra) [a](Extra Plus)	113.35±1.40	115.88±1.05 (+2.23%)	117.16±1.13 (+3.36%)	115.59±1.04 (+1.98%)	0.41	0.62
Plus (saving) [a](Saving Plus)	113.35±1.40	114.94±1.03 (+1.40%)	119.76±1.13 (+5.66%)	117.00±0.85 (+3.31%)	NS	NS
Rin Shakti	113.35±1.40	116.42±1.58 (+2.69%)	115.70±1.13 (+2.07%)	113.58±1.70 (+0.20%)	0.93	1.40
Rin Supreme	113.35±1.40	125.32±1.27 (+10.96%)	118.90±1.12 (+4.90%)	116.48±1.05 (+2.76%)	0.38	0.57
Surf	113.35±1.40	117.16±1.24 (+3.36%)	126.37±1.29 (+11.49%)	114.25±1.59 (+0.8%)	0.90	1.36
Surf Excel	113.35±1.40	119.81±1.12 (+5.70%)	126.43±1.20 (+11.54%)	115.06±0.96 (+1.51%)	0.45	0.68
Tide	113.35±1.40	121.07±1.16 (+6.81%)	116.08±1.07 (+2.41%)	113.76±1.17 (+0.37%)	1.33	2.01
Time-Zee	113.35±1.40	117.09±1.01 (+3.30%)	114.56±1.09 (+1.07%)	114.94±1.33 (+1.41%)	NS	NS
Wheel	113.35±1.40	115.52±1.47 (+1.91%)	121.82±0.89 (+7.47%)	113.58±0.96 (+0.20%)	0.73	1.10

Mean ± SD, with in parenthesis-per cent variation over the control
[a] Actual brand name

Table 12.7 Dry weight (mg/g of fresh weight) of *Spirodela polyrrhiza* treated in small plastic pots with varying doses of 12 selected detergent cakes

Detergent (Brand name)	Control	Concentration (ppm)			LSD at	
	0	10	30	50	5%	1%
Ariel	113.75±1.16	117.91±2.01 (+3.66%)	121.96±2.07 (+7.22%)	119.56±1.40 (+5.11%)	4.49	6.81
Budget	113.75±1.16	117.99±1.97 (+3.72%)	115.77±1.56 (+1.76%)	113.80±1.18 (+0.04%)	NS	NS
Doctor	113.75±1.16	117.80±1.32 (+3.56%)	118.92±0.97 (+4.55%)	116.50±1.50 (+2.42%)	2.84	4.29
Fena	113.75±1.16	121.68±1.98 (+6.97%)	117.57±1.58 (+3.36%)	115.50±1.73 (+1.54%)	4.60	6.95
555	113.75±1.16	116.58±2.02 (+2.49%)	121.66±1.18 (+6.95%)	118.86±0.91 (+4.49%)	3.82	5.79
Ghari	113.75±1.16	114.88±1.19 (+0.99%)	118.32±1.12 (+4.02%)	116.54±0.88 (+2.45%)	2.71	4.10
Henko	113.75±1.16	117.67±1.57 (+3.45%)	119.22±1.12 (+4.81%)	123.55±1.24 (+8.62%)	2.68	4.06
Mor	113.75±1.16	114.80±0.97 (+0.09)	118.60±1.47 (+4.26%)	116.80±1.28 (+2.68%)	3.16	4.80
Nirma	113.75±1.16	116.58±1.76 (+2.49%)	121.66±1.76 (+6.95%)	118.86±1.21 (+4.49%)	3.16	4.78
Plus	113.75±1.16	115.50±1.05 (+1.54%)	116.77±1.76 (+2.65%)	119.68±2.10 (+5.93%)	NS	NS
Rin	113.75±1.16	118.93±2.02 (+4.55%)	120.86±1.98 (+6.25%)	124.19±1.46 (+9.19%)	4.40	6.67
Wheel	113.75±1.16	118.53±1.69 (+4.20%)	123.86±1.41 (+8.89%)	120.76±2.07 (+6.16%)	4.50	6.82

Mea ± SD, with in parenthesis percent variation over the control

Table 12.8 comprises the data on dry weight of *Spirodela polyrrhiza* treated in small plastic pots with varying concentrations of 24 selected detergent powders. A glance on the Table 12.8 revealed that the impact of detergent powders on dry weight of *Spirodela polyrrhiza* was higher than the impact of all 12 selected detergent cakes. The *Spirodela polyrrhiza* treated with Ariel detergent powder showed maximum dry weight accumulation at 30 ppm as compared to the control (0 ppm). The impact of Double Dog detergent powder on dry weight was far lesser than the impact of Ariel. The high concentration (50 ppm) of the detergents like Fena, Ghari, Nirma, Nirma Super, and Rin Supreme significantly

Table 12.8 Dry weight (mg/g of fresh weight) of *Spirodela polyrrhiza* treated in small plastic pots with varying doses of 24 selected detergent powders

Detergent (Brand name)	Control	Concentration (ppm)			LSD at	
	0	10	30	50	5%	1%
Ariel	113.45±1.83	119.74±1.80 (+5.54%)	124.82±2.21 (+10.02%)	121.36±2.38 (+6.97%)	5.85	8.86
Cleano	113.45±1.83	117.67±2.20 (+3.72%)	116.95±2.05 (+3.09%)	114.72±1.20 (+1.12%)	NS	NS
Doctor	113.45±1.83	114.98±1.33 (+1.35%)	115.95±2.11 (+2.20%)	117.93±1.27 (+3.95%)	NS	NS
Double Dog	113.45±1.83	125.83±1.94 (+10.91%)	122.20±1.71 (+7.71%)	120.79±1.90 (+6.47%)	5.21	7.89
Fena	113.45±1.83	115.50±1.51 (+1.81%)	117.57±1.87 (+3.63%)	121.68±1.98 (+7.25%)	5.10	7.72
Friendly wash	113.45±1.83	125.38±1.59 (+10.52%)	122.96±2.31 (+8.38%)	120.54±2.33 (+6.25%)	5.76	8.73
Ghari	113.45±1.83	117.08±1.89 (+3.20%)	118.13±2.19 (+4.13%)	123.50±1.92 (+8.86%)	5.54	8.39
Henko	113.45±1.83	119.99±2.09 (+5.76%)	125.98±2.11 (+11.04%)	122.20±2.40 (+7.71%)	5.97	9.04
Max Clean	113.45±1.83	114.68±1.71 (+1.08%)	117.52±2.26 (+3.59%)	114.21±1.71 (+0.67%)	NS	NS
Mor	113.45±1.83	117.73±1.80 (+3.77%)	121.12±1.83 (+6.76%)	115.25±2.19 (+1.59%)	NS	NS
Mor light	113.45±1.83	116.81±1.76 (+2.96%)	118.59±2.32 (+4.53%)	115.14±2.42 (+1.49%)	NS	NS
Mr. white	113.45±1.83	125.09±2.20 (+10.26%)	120.65±2.18 (+6.35%)	120.80±2.41 (+6.49%)	6.10	9.24
Nirma	113.45±1.83	117.91±1.26 (+3.93%)	118.79±1.80 (+4.71%)	124.39±1.85 (+9.64%)	4.80	7.27
Nirma (Super) [a](Super Nirma)	113.45±1.83	115.15±1.89 (+1.50%)	120.60±1.40 (+6.30%)	124.00±2.54 (+9.30%)	5.47	8.28
Plus	113.45±1.83	115.37±1.92 (+1.69%)	115.10±2.56 (+1.45%)	120.52±2.39 (+6.23%)	NS	NS
Plus (extra) [a](extra plus)	113.45±1.83	115.84±1.40 (+2.12%)	120.42±1.80 (+6.14%)	114.06±2.52 (+0.54%)	NS	NS
Plus (saving) [a](saving plus)	113.45±1.83	115.00±2.24 (+1.37%)	122.89±2.56 (+8.32%)	117.27±2.43 (+3.37%)	6.44	9.76
Rin Shakti	113.45±1.83	119.07±2.61 (+5.0%)	124.83±2.33 (+10.03%)	119.79±2.58 (+5.59%)	6.62	10.03
Rin Supreme	113.45±1.83	122.27±2.22 (+7.77%)	122.16±2.41 (+7.68%)	125.73±2.04 (+10.82%)	5.45	8.25
Surf	113.45±1.83	117.33±1.54 (+3.42%)	126.42±2.01 (+11.43%)	122.57±2.07 (+8.04%)	5.29	8.02
Surf Excel	113.45±1.83	120.54±1.82 (+6.25%)	126.58±2.16 (+11.57%)	122.96±1.23 (+8.38%)	5.02	7.60
Tide	113.45±1.83	119.65±1.89 (+5.46%)	124.64±1.96 (+9.86%)	116.50±2.14 (+2.69%)	5.53	8.38
Time-Zee	113.45±1.83	114.87±2.13 (+1.25%)	115.56±1.83 (+1.86%)	119.45±1.85 (+5.29%)	NS	NS
Wheel	113.45±1.83	121.35±1.67 (+6.96%)	117.26±2.21 (+3.36%)	114.85±2.11 (+1.23%)	NS	NS

Mean±SD, within parenthesis percent variation over the control
[a] Actual brand name

enhanced the dry weight of *Spirodela polyrrhiza* as compared to 0, 10, and 30 ppm. The dry weight of *Spirodela polyrrhiza* increased significantly on treatment with 30 ppm of Friendly Wash, Henko, Saving Plus, Rin Shakti, Surf, and its new brand Surf Excel powder. The impact of Surf and Surf Excel was highest than the other detergents powder under study. The dry weight of *Spirodela polyrrhiza* statistically did not vary on treatment with varying concentrations of Cleano, Doctor, Maxclean, Mor, Morlight, Plus, Plus Extra, Time-zee, and Wheel detergent powders (Table 12.8).

12.3.4 Duckweed Response to Surf Excel Detergent in 15 L Earthen Pots

12.3.4.1 Growth Responses of *Lemna minor*

Table 12.9 comprises the data on the growth responses of *Lemna minor* treated with varying concentrations of Surf Excel in large earthen pots and studied at11th day. The statistical analysis of the data revealed that the dry weight per gram fresh plant of *Lemna minor* significantly increased on treatment with 20, 30, 40, and 50 ppm of Surf Excel. The lower concentrations of Surf Excel increased chlorophyll *a* and *b*. The nitrogen content in the plants treated with varying concentrations of Surf Excel had for greater amount of nitrogen than the control. There was a marginal but significant increase in phosphorus uptake in *Lemna minor* treated with varying concentrations of Surf Excel as compared to control plant. The phosphorus uptake was, however, highest at 20 ppm of Surf Excel. A significant increase in potassium uptake was recorded at higher concentrations of Surf Excel. Nitrogen uptake in plant increased up to 30 ppm concentration level and declined with further increase in the concentration of the detergent (Table 12.9).

12.3.4.2 Water Quality

The data on the physico–chemical properties of water samples of earthen pots studied at 11th-day stage are summarized in Table 12.10.The data show that the pH and turbidity consistently increased with the concentration in earthen pots. The dissolved oxygen (except some variations at 40 ppm level) reduced with the increase in concentration of Surf Excel. The nitrate contents decreased marginally with the increase in Surf Excel concentration. Despite significant uptake, the high amounts of phosphates (in proportion to concentration of detergent) accumulated in the solutions of Surf

Table 12.9 Growth response of *Lemna minor* treated in large earthen pots with varying concentrations of Surf Excel detergent

Parameters	Concentration (ppm)						LSD at	
	0	10	20	30	40	50	5%	1%
Dry weight (mg/g)	117.2±2.6	119.2±2.1 (+1.7%)	128.1±2.2 (+9.3%)	124.1±1.4 (+5.9%)	122.7±1.3 (+4.7%)	122.0±2.0 (+4.1%)	3.0	4.6
Chlorophyll-a (mg/g)	0.61±0.04	0.66±0.03 (+7.3%)	0.74±0.05 (+19.8%)	0.62±0.04 (+1.1%)	0.68±0.05 (+10.1%)	0.64±0.08 (+4.6%)	0.04	0.07
Chlorophyll-b (mg/g)	0.32±0.05	0.36±0.02 (+11.2%)	0.41±0.08 (+28.0%)	0.33±0.03 (+2.5%)	0.37±0.04 (+15.3%)	0.34±0.03 (+4.7%)	0.05	0.08
Chlorophyll total (mg/g)	1.00±0.04	1.07±0.07 (+6.3%)	1.19±0.09 (+18.1%)	1.04±0.07 (+3.6%)	1.07±0.06 (+6.1%)	1.07±0.07 (+6.3%)	0.06	0.09
Nitrogen (mg/100 mg)	2.68±0.22	3.18±0.19 (+18.7%)	3.39±0.19 (+26.4%)	3.65±0.25 (+36.2%)	3.22±0.24 (+20.2%)	2.96±0.29 (+10.5%)	0.28	0.56
Phosphorus (mg/100 mg)	0.30±0.04	0.38±0.05 (+27.0%)	0.41±0.02 (+37.3%)	0.39±0.04 (+28.6%)	0.37±0.03 (+24.0%)	0.37±0.04 (+22.6%)	0.02	0.05
Potassium (mg/100 mg)	1.73±0.28	1.86±0.28 (+7.5%)	1.76±0.38 (+1.7%)	1.90±0.32 (+9.8%)	2.3±0.33 (+33.0%)	2.10±0.41 (+21.4%)	0.26	0.46

Mean ± SD, within parenthesis percent increase over the control (in rounded figures)

Table 12.10 Physico–chemical characteristics of varying concentrations of Surf Excel detergent solutions including control as estimated after the experiments with *Lemna minor* 15 L earthen pots

Parameters	Concentration (ppm)						LSD at	
	0	10	20	30	40	50	5%	1%
Turbidity (NTU)	9±2	11±3 (+22.22%)	14±2 (+55.56%)	16±2 (+77.78%)	18±2 (+100%)	19±3 (+111.11%)	3.2	4.6
pH	7.6±0.1	7.7±0.1 (+1.32%)	7.9±0.2 (+3.95%)	8.1±0.1 (+6.58%)	8.5±0.2 (+11.84%)	8.8±0.2 (+15.79%)	0.3	0.4
Dissolved oxygen (mg L^{-1})	7.45±0.45	7.12±0.27 (−4.43%)	6.83±0.28 (−8.32%)	5.69±0.41 (−23.62%)	6.09±0.26 (−18.26%)	5.45±0.30 (−26.85%)	0.17	0.24
Nitrates (mg L^{-1})	±.423±0.022	0.407±0.062 (−3.75%)	0.399±0.050 (−5.60%)	0.38±0.068 (−9.69%)	0.404±0.085 (−4.49%)	0.416±0.040 (−1.42%)	0.016	0.022
Phosphates (mg L^{-1})	±.618±0.106	0.932±0.115 (+50.81%)	1.198±0.299 (+93.85%)	1.498±0.320 (+142.39%)	1.814±0.340 (+193.53%)	2.083±0.279 (+237.06%)	0.157	0.216
Potassium (mg L^{-1})	13.60±1.10	13.15±1.11 (−3.31%)	13.09±1.20 (−3.75%)	13.16±1.15 (−3.24%)	13.06±1.02 (−3.97%)	13.26±1.10 (−2.50%)	0.957	1.379

Mean ± SD, within parenthesis percent variation over the control

Excel. There was no statistical difference in potassium level in all treatments including control (Table 12.10).

12.3.4.3 Growth Responses of *Spirodela polyrrhiza*

Table 12.11 shows the data on the growth responses of *Spirodela polyrrhiza*treated in large earthen pots with varying concentrations of Surf Excel powder. As evident from data the *Spirodela polyrrhiza* grown in varying concentrations of Surf Excel accumulated larger amount of dry matter as compared to the control. The chlorophyll *a* and *b* in the plants treated with Surf Excel was marginally higher. The chlorophyll *a* and *b* in plant treated with 40 ppm of Surf Excel was relatively higher than in any other treatment. The nitrogen, phosphorus, and potash uptake was found related with concentrations of Surf Excel up to 40 ppm. The uptake of NPK showed consistent increase with the detergent concentration up to 40 ppm with some exception of nitrogen uptake (Table 12.11).

12.3.4.4 Water Quality

The data summarized in Table 12.12 show the physico–chemical properties of the water sampled from varying concentrations of Surf Excel. The turbidity and pH increased with the concentration of the detergent used. The dissolved oxygen was negatively related with the detergent concentration. After the treatment, the nitrate content in solution with higher detergent concentrations significantly reduced as compared to control. The phosphate was found almost directly related with the concentration of Surf Excel. Potassium, however, did not show any statistical difference in all water samples ranging from 0 to 50 ppm of Surf Excel (Table 12.12).

Table 12.11 Growth response of *Spirodela polyrrhiza* treated in large earthen pots with varying concentrations of Surf Excel detergent powder

Parameters	Concentration (ppm)						LSD at	
	0	10	20	30	40	50	5%	1%
Dry weight (mg/g)	122.3±1.8	125.9±1.3 (+2.9%)	124.2±2.2 (+1.6%)	125.0±2.4 (+2.2%)	131.5±2.1 (+7.5%)	127.6±2.1 (+4.3%)	2.9	4.2
Chlorophyll-a (mg/g)	0.63±0.25	0.64±0.23 (+0.8%)	0.64±0.28 (+1.4%)	0.70±0.02 (+11.2%)	0.79±0.01 (+24.2%)	0.72±0.2 (+13.9%)	0.03	0.04
Chlorophyll-b (mg/g)	0.35±0.01	0.37±0.02 (+4.0%)	0.36±0.02 (+3.0%)	0.38±0.02 (+8.3%)	0.44±0.02 (+25.9%)	0.39±0.02 (+12.0%)	0.02	0.05
Chlorophyll total (mg/g)	0.99±0.02	1.03±0.02 (+3.9%)	1.02±0.05 (+2.9%)	1.12±0.04 (+13.1%)	1.30±0.04 (+31.0%)	1.12±0.01 (+12.18%)	0.05	0.07
Nitrogen (mg/100 mg)	3.09±0.15	3.39±0.18 (+9.7%)	4.13±0.19 (+33.7%)	3.69±0.20 (+19.4%)	3.64±0.20 (+17.8%)	3.80±0.17 (+23.0%)	0.13	0.25
Phosphorus (mg/100 mg)	0.25±0.03	0.34±0.02 (+36.7%)	0.37±0.02 (+45.8%)	0.39±0.02 (+53.4%)	0.40±0.27 (+59.8%)	0.35±0.22 (+39.4%)	0.01	0.03
Potassium (mg/100 mg)	2.20±0.18	2.24±0.15 (+1.8%)	2.33±0.28 (+5.9%)	2.37±0.17 (+7.7%)	2.70±0.22 (+22.7%)	2.40±0.13 (+9.1%)	0.16	0.23

Mean ± SD, within parenthesis percent increase over the control (in rounded figures)

Table 12.12 Physico–chemical characteristics of varying concentrations of Surf Excel detergent including control as estimated after the experiments with *Spirodela polyrrhiza* in 15 L earthen pots

Parameters	Concentration (ppm)						LSD at	
	0	10	20	30	40	50	5%	1%
Turbidity (NTU)	12±2.0	14±3.6 (+16.7%)	16±4.4 (+33.3%)	19±0.0 (+28.3%)	21±2.5 (+75.0%)	22±3.0 (+83.3%)	5.17	7.35
pH	7.5±0.3	7.7±0.4 (+2.67%)	7.8±0.3 (+4.0%)	8.0±0.4 (+6.67%)	8.3±0.2 (+10.66%)	8.5±0.3 (+13.33%)	0.4	0.6
Dissolved oxygen (mg L^{-1})	7.52±0.08	7.22±0.15 (−3.99%)	6.62±0.32 (−11.97%)	6.38±0.13 (−15.14%)	5.93±0.25 (−21.11%)	5.79±0.41 (−23.03%)	0.19	0.28
Nitrates (mg L^{-1})	±0.465±0.033	0.435±0.048 (−6.45%)	0.349±0.040 (−24.95%)	0.396±0.064 (−14.84%)	0.379±0.63 (-18.49%)	0.404±0.076 (−13.12%)	0.045	0.061
Phosphates (mg L^{-1})	±0.597±0.036	0.899±0.067 (+50.59%)	1.455±0.083 (+143.72%)	1.550±0.146 (+160.00%)	1.786±0.176 (+199.16%)	2.065±0.222 (+245.90%)	0.147	0.210
Potassium (mg L^{-1})	13.22±0.41	13.15±0.41 (−0.53%)	13.12±1.00 (−0.76%)	13.0±0.16 (−1.66%)	13.12±0.21 (−0.76%)	13.21±0.20 (−0.08%)	NS	NS

Mean±SD, within parenthesis percent variation over the control

12.3.5 Effect of Temperature

12.3.5.1 Sensitivity of *Lemna minor*

The data on dry weight, chlorophyll content and NPK of *Lemna minor* recorded at 11th day of treatment or after their death (at an early stage in response to high temperatures) are summarized in Table 12.13. The greater quantity of matter accumulation was noted on treatment with 30 and 40 ppm of Surf Excel at 20 and 30 °C temperatures. The nitrogen accumulation was optimum at 30 °C in the plants treated with 30 and 40 ppm of Surf Excel. The optimum uptake of phosphorus was noted on treatment with 50 ppm of Surf Excel at 20 °C temperature. The most noticeable changes in phosphorus uptake were recorded in almost all treatments maintained at 20 and 30 °C temperatures. The potassium uptake was also significantly higher in most of the treatments at 20, 30, and 40 °C. The optimum uptake in potassium was recorded in plants treated with 40 ppm of Surf Excel at 20 °C temperature (Table 12.13).

12.3.5.2 Water Quality

The data summarized in the Table 12.14 show the physico–chemical characteristics of the water samples with varying concentrations of Surf Excel maintained at five temperature ranges and studied at 11th day of growth experiments with of *Lemna minor*. The pH and turbidity of water shows marginal but consistent increase with the detergent concentration at all temperature regimes. The dissolved oxygen reduced significantly in almost all treatments of Surf Excel with respect to control at 20 and 30 °C temperature. No significant difference in accumulation of nitrates was recorded between all the treatments. The interaction of temperature and treatment also did not show any statistical difference. The phosphates

Table 12.13 Growth response of *Lemna minor* treated in small plastic pots with varying concentrations of Surf Excel at varying temperatures

Parameters	Temperature (°C)	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Dry weight (mg/g)	10	117.05±1.25	119.98±1.78 (+2.50%)	117.65±2.65 (+0.51%)	118.65±3.15 (+1.37%)	121.15±1.55 (+3.50%)	120.31±2.84 (+2.79%)	
	20	115.31±2.36	115.48±1.69 (+0.15%)	123.45±2.45 (+7.06%)	122.35±2.48 (+6.11%)	125.15±2.25 (+8.54%)	121.35±2.84 (+5.24%)	Treatment=1.89
	30	119.25±1.90	121.65±1.19 (+2.01%)	120.25±1.95 (+0.84%)	124.55±3.65 (+4.44%)	129.15±3.25 (+8.30%)	119.43±3.09 (+0.15%)	Temperature=1.72
	40[a]	92.27±2.67	91.23±2.48 (−1.12%)	93.97±3.20 (+1.84%)	92.33±1.53 (+0.65%)	95.99±3.32 (+4.01%)	93.13±2.38 (+0.93%)	Interaction=4.22
	50[b]	76.15±2.20	75.35±2.80 (−1.05%)	76.55±1.69 (+0.53%)	77.15±2.62 (+1.27%)	76.92±3.62 (+1.01%)	77.36±1.56 (+1.59%)	
Chlorophyll-a (mg/g)	10	0.563±0.012	0.610±0.022 (+8.35%)	0.575±0.014 (+2.13%)	0.653±0.025 (+15.99%)	0.621±0.020 (+10.30%)	0.582±0.023 (+3.37%)	
	20	0.586±0.021	0.649±0.028 (+10.75%)	0604±0.029 (+6.34%)	0.722±0.021 (+27.11%)	0.658±0.025 (+15.84%)	0.632±0.022 (+11.27%)	Treatment=0.023
	30	0.572±0.013	0.675±0.016 (+18.01%)	0.622±0.021 (+8.74%)	0.699±0.022 (+22.20%)	0.689±0.024 (+20.45%)	0.608±0.024 (+6.29%)	Temperature=0.015
	40[a]	0.482±0.016	0.448±0.019 (+7.05%)	0.505±0.016 (+4.77%)	0.491±0.032 (+1.87%)	0.484±0.020 (+0.41%)	0.487±0.024 (+1.04%)	Interaction=0.038
	50[b]	0.436±0.017	0.449±0.024 (+14.44%)	0.445±0.018 (+2.06%)	0.454±0.023 (+4.13%)	0.515±0.025 (+18.12%)	0.440±0.032 (+0.92%)	
Chlorophyll-b (mg/g)	10	0.233±0.027	0.254±0.023 (+9.01%)	0.237±0.043 (+1.72%)	0.275±0.026 (+18.03%)	0.262±0.023 (+12.45%)	0.248±0.023 (+6.44%)	
	20	0.254±0.019	0.355±0.017 (+39.76%)	0.268±0.023 (+5.51%)	0.370±0.020 (+45.67%)	0.317±0.022 (+24.80%)	0.271±0.026 (+6.69%)	Treatment=0.017
	30	0.275±0.019	0.307±0.032 (+11.64%)	0.305±0.022 (+10.91%)	0.417±0.028 (+51.64%)	0.360±0.012 (+30.90%)	0.321±0.020 (+16.73%)	Temperature=0.015
	40[a]	0.169±0.024	0.185±0.015 (+9.46%)	0.177±0.017 (+4.73%)	0.175±0.028 (+3.55%)	0.181±0.030 (+7.10%)	0.172±0.023 (+1.78%)	Interaction=0.038
	50[b]	0.189±0.018	0.176±0.022 (−7.41%)	0.173±0.014 (−8.47%)	0.192±0.021 (+1.59%)	0.177±0.019 (−6.35%)	0.199±0.030 (+5.29%)	
Total chlorophyll (mg/g)	10	0.844±0.023	0.916±0.101 (+8.53%)	0.890±0.056 (+5.45%)	1.034±0.034 (+22.51%)	0.888±0.027 (+5.21%)	0.870±0.130 (+3.08%)	
	20	0.874±0.021	1.064±0.050 (+8.53%)	0.931±0.036 (+6.52%)	1.208±0.103 (+38.22%)	1.027±0.034 (+17.51%)	0.905±0.025 (+3.55%)	Treatment=0.045
	30	0.909±0.028	1.022±0.033 (+12.43%)	0.973±0.028 (+7.04%)	1.168±0.089 (+28.49%)	1.071±0.086 (+17.82%)	0.945±0.138 (+3.96%)	Temperature=0.041
	40[a]	0.632±0.023	0.719±0.042 (+13.76%)	0.652±0.027 (+3.16%)	0.688±0.057 (+8.86%)	0.679±0.046 (+7.44%)	0.673±0.012 (+6.49%)	Interaction=0.100
	50[b]	0.507±0.034	0.526±0.037 (+3.74%)	0.516±0.037 (+1.78%)	0.527±0.038 (+3.94%)	0.538±0.039 (+6.11%)	0.514±0.024 (+1.38%)	
Nitrogen (mg/100 mg)	10	2.70±0.31	2.88±0.56 (+6.73%)	3.10±0.25 (+14.58%)	3.03±0.28 (+12.13%)	2.92±0.48 (+7.92%)	2.86±0.44 (+5.95%)	
	20	2.89±0.45	2.74±0.31 (+5.33%)	2.95±0.51 (+1.94%)	3.42±0.49 (+18.26%)	3.18±0.43 (+9.82%)	2.90±0.58 (+0.21%)	Treatment=NS
	30	3.08±0.19	3.33±0.24 (+7.92%)	3.25±0.21 (+5.32%)	3.71±0.74 (+20.38%)	3.44±0.33 (+11.49%)	3.25±0.45 (+5.52%)	Temperature=0.28
	40[a]	2.31±0.21	2.64±0.44 (+14.40%)	2.39±0.39 (+3.56%)	2.51±0.36 (+8.85%)	2.46±0.47 (+6.59%)	2.53±0.30 (+9.80%)	Interaction=0.67
	50[b]	2.04±0.15	2.01±0.06 (−1.67%)	2.04±0.40 (+0.05%)	2.12±0.37 (+3.82%)	2.03±0.50 (−0.69%)	2.03±0.14 (−0.54%)	
Phosphorus (mg/100 mg)	10	0.215±0.027	0.219±0.039 (+1.86%)	0.215±0.015 (+0.0%)	0.232±0.043 (+7.91%)	0.224±0.016 (+4.19%)	0.288±0.031 (+6.05%)	
	20	0.231±0.030	0.260±0.023 (+12.55%)	0.274±0.021 (+18.61%)	0.304±0.023 (+31.60%)	0.289±0.014 (+25.11%)	0.324±0.023 (+40.26%)	Treatment=NS
	30	0.257±0.017	0.298±0.051 (+15.95%)	0.238±0.029 (+7.39%)	0.355±0.027 (+38.13%)	0.338±0.035 (+31.52%)	0.280±0.045 (+8.95%)	Temperature=0.020
	40[a]	0.207±0.022	0.228±0.018 (+10.14%)	0.217±0.028 (+4.83%)	0.244±0.027 (+17.87%)	0.254±0.026 (+22.20%)	0.217±0.032 (+4.83%)	Interaction=0.044
	50[b]	0.177±0.032	0.186±0.080 (+5.08%)	0.181±0.022 (+2.26%)	0.200±0.027 (+12.99%)	0.196±0.029 (+10.73%)	0.191±0.020 (+7.91%)	
Potassium (mg/100 mg)	10	1.50±0.38	1.56±0.16 (+4.02%)	1.58±0.19 (+5.78%)	1.52±0.260 (+1.54%)	1.56±0.21 (+4.21%)	1.74±0.25 (+16.44%)	
	20	1.85±0.17	2.02±0.21 (+9.44%)	2.06±0.28 (+11.53%)	1.85±0.27 (+0.22%)	2.23±0.23 (+20.84%)	1.86±0.12 (+0.65%)	Treatment=NS
	30	1.70±0.19	1.60±0.31 (+6.22%)	1.85±0.21 (+8.57%)	1.97±0.20 (+15.55%)	2.00±0.19 (+17.37%)	1.98±0.30 (+16.37%)	Temperature=0.14
	40[a]	1.21±0.16	1.23±0.12 (+1.82%)	1.42±0.31 (+17.58%)	1.28±0.18 (+6.22%)	1.32±0.23 (+9.78%)	1.54±0.20 (+27.86%)	Interaction=0.35
	50[b]	1.04±0.05	1.04±0.05 (+0.30%)	1.06±0.07 (+1.83%)	1.11±0.10 (+6.24%)	1.08±0.09 (+3.75%)	1.07±0.09 (+2.52%)	

Mean±SD, with in parenthesis percent variation over the control

[a] Studied in samples collected at seventh day after the death of plants

[b] Studied in samples collected at fifth day after the death of plant

Table 12.14 Physico–chemical characteristics of water containing varying concentration of surf excel detergent maintained at varying temperature studied after 11th day of growth of *Lemna minor*

Parameters	Temperature (°C)	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Turbidity (NTU)	10	10±1	11±1 (+10%)	13±1 (+30%)	14±1 (+40%)	15±3 (+50%)	16±1 (+60%)	
	20	11±2	12±1 (+9.09%)	12±2 (+9.09%)	15±1 (+36.36%)	16±2 (+45.45%)	17±2 (+55.55%)	Treatment = 1.74
	30	13±2	14±2 (+7.69%)	16±1 (+23.17%)	18±2 (+46.15%)	20.0±3 (+53.85%)	22±1 (+69.23%)	Temperature = 1.58
	40[a]	15±2	17±1 (+13.33%)	19±3 (+26.67%)	19±3 (+26.67%)	21±4 (+40.0%)	22±1 (+46.66%)	Interaction = 3.88
	50[b]	17±3	18±2 (+5.88%)	20.0±4 (+17.64%)	21±2 (+23.53%)	21±1 (+23.53%)	23±5 (+35.29%)	
pH	10	7.4±0.3	7.5±0.4 (+1.35%)	7.7±0.3 (+4.05%)	7.9±0.3 (+6.76%)	8.0±0.3 (+8.11%)	8.2±0.2 (+10.81%)	
	20	7.5±0.3	7.7±0.3 (+2.67%)	7.8±0.4 (+4.0%)	8.1±0.2 (+8.00%)	8.3±0.1 (+10.67%)	8.4±0.1 (+12.0%)	Treatment = 0.22
	30	7.5±0.4	7.6±0.2 (+1.33%)	7.8±0.4 (+4.0%)	8.2±0.1 (+9.33%)	8.4±0.3 (+12.0%)	8.5±0.5 (+13.33%)	Temperature = 0.20
	40[a]	7.7±0.2	7.9±0.4 (+2.60%)	8.2±0.3 (+6.49%)	8.3±0.2 (+7.79%)	8.5±0.2 (+10.39%)	8.7±0.2 (+12.99%)	Interaction = 0.49
	50[b]	7.6±0.3	7.8±0.4 (+2.63%)	8.1±0.4 (+6.58%)	8.3±0.1 (+11.84%)	8.5±0.11 (+11.84%)	8.6±0.4 (+13.15%)	
Dissolved oxygen (mg L^{-1})	10	7.47±0.32	6.76±0.21 (−9.50%)	7.03±0.22 (−5.89%)	6.52±0.34 (−12.72%)	6.65±0.24 (−10.98%)	6.49±0.18 (−13.12%)	
	20	7.90±0.11	7.50±0.40 (−5.06%)	6.78±0.16 (−14.18%)	6.65±0.25 (−15.82%)	5.08±0.24 (−39.70%)	6.00±0.10 (−24.05%)	Treatment = 0.19
	30	7.33±0.35	6.47±0.22 (−11.73%)	6.95±0.15 (−5.18%)	5.70±0.16 (−22.24%)	5.18±0.27 (−29.33%)	5.47±0.17 (−25.40%)	Temperature = 0.17
	40[a]	7.07±0.22	6.31±0.12 (−10.75%)	7.35±0.25 (−3.96%)	6.98±0.26 (−1.27%)	6.73±0.22 (−4.81%)	6.55±0.34 (−7.35%)	Interaction = 0.42
	50[b]	7.60±0.15	6.87±0.15 (−9.61%)	7.43±0.23 (−2.24%)	7.22±0.37 (−5.0%)	7.21±0.34 (−5.13%)	7.06±0.26 (−7.11%)	
Nitrates (mg L^{-1})	10	0.742±0.033	0.736±0.045 (−0.81%)	0.724±0.074 (−2.43%)	0.728±0.028 (−1.89%)	0.738±0.017 (−0.54%)	0.725±0.054 (−2.29%)	
	20	0.734±0.049	0.717±0.029 (−2.32%)	0.669±0.070 (−8.86%)	0.642±0.072 (−12.53%)	0.733±0.030 (−0.14%)	0.724±0.059 (−1.36%)	Treatment = NS
	30	0.703±0.028	0.653±0.044 (−7.11%)	0.613±0.035 (−12.80%)	0−685±0.065 (−2.56%)	0.683±0.028 (−2.84%)	0.669±0.080 (−4.83%)	Temperature = 0.038
	40[a]	0.723±0.030	0.695±0.145 (−3.87%)	0.715±0.051 (−1.12%)	0.705±0.028 (−2.44%)	0.742±0.028 (−2.63%)	0.705±0.035 (−2.49%)	Interaction = 0.093
	50[b]	0.749±0.023	0.741±0.076 (−1.07%)	0.693±0.088 (−7.48%)	0.740±0.038 (−1.07%)	0.739±0.018 (−1.34%)	0.740±0.05 (−1.20%)	
Phosphates (mg L^{-1})	10	0.630±0.040	1.043±0.056 (+65.56%)	1.426±0.219 (+126.35%)	1.782±0.557 (+182.86%)	2.093±0.128 (+232.22%)	2.330±0.341 (+269.84%)	
	20	0.590±0.060	1.066±0.091 (+80.68%)	1.434±0.048 (+143.05%)	1.726±0.522 (+192.54%)	2.040±0.145 (+245.76%)	2.274±0.379 (+285.42%)	Treatment = 0.211
	30	0.610±0.05	1.096±0.116 (+79.67%)	1.371±0.376 (+124.75%)	1.688±0.388 (+176.72%)	2.063±0.129 (+238.20%)	2.310±0.335 (+278.69%)	Temperature = 0.193
	40[a]	0.620±0.020	1.075±0.100 (+73.39%)	1.402±0.402 (+126.13%)	1.754±0.359 (+182.90%)	2.058±0.193 (+231.94%)	2.322±0.322 (+274.52%)	Interaction = 0.472
	50[b]	0.630±0.040	1.080±0.089 (+71.43%)	1.443±0.257 (+129.05%)	1.745±0.295 (+176.98%)	2.004±0.113 (+218.10%)	2.359±0.309 (+274.44%)	
Potassium (mg L^{-1})	10	13.69±0.49	13.52±0.83 (−1.24%)	13.39±0.59 (−2.19%)	13.56±0.74 (−0.95%)	13.41±1.26 (−2.05%)	13.55±1.10 (−1.02%)	
	20	13.54±0.53	13.52±0.83 (−0.15%)	13.34±0.38 (−2.56%)	13.52±0.52 (−1.24%)	13.42±1.23 (−1.97%)	13.22±0.41 (−1.24%)	Treatment = 0.04
	30	13.58±0.58	13.45±0.59 (−0.96%)	13.35±0.35 (−1.69%)	13.48±0.27 (−0.74%)	13.48±0.62 (−1.97%)	13.42±1.11 (−1.18%)	Temperature = NS
	40[a]	13.68±1.24	13.52±0.61 (−1.17%)	13.48±0.65 (−1.46%)	13.51±0.71 (−1.24%)	13.43±0.89 (−1.83%)	13.52±0.95 (−1.17%)	Interaction = NS
	50[b]	13.54±0.55	13.50±0.48 (−0.30%)	13.39±0.62 (−1.11%)	13.51±0.64 (−0.22%)	13.44±0.94 (−0.74%)	13.44± (−0.74%)	

Mean ± SD, with in parenthesis percent variation over the control

[a] Studied in samples collected at seventh day after the death of plants

[b] Studied in samples collected at fifth day after the death of plants

were significantly high and the quantity consistently increased with the concentration of Surf Excel. The phosphate accumulation of water was statistically found directly related with temperature. With one exception there was no statistical difference in potassium accumulation in all treatments including control. Similarly temperature also did not affect the potassium content of the solution. It was noticeable that the *Lemna minor* had high mortality in higher concentration and temperature levels (Table 12.14).

12.3.5.3 Sensitivity of *Spirodela polyrrhiza*

The data summarized in Table 12.15 show the growth response of *Spirodela polyrrhiza* treated in small pots with varying concentration of Surf Excel at varying temperatures. The dry weight accumulation significantly decreased in *Spirodela polyrrhiza* maintained at 40 and 50 °C in all treatments levels. The dry weight accumulation of *Spirodela polyrrhiza* was, however, statistically similar in all concentrations maintained at 10, 20, and 30 °C. Significant reductions in dry weight and chlorophyll content were noted in all treatments maintained at 40 and 50 °C temperature (as recorded in the samples collected either on 5th day, 9th day or after the termination of the experiment at 11th day). Nitrogen uptake was optimum in 40 ppm concentration at 20 and 30 °C. Significantly a higher amount of phosphorous uptake was recorded at 20 and 30 °C temperatures in all doses of Surf Excel. The uptake of phosphorous was also relatively higher in all concentrations of Surf Excel at 10 °C but the uptake of phosphorous did not show any significant decrease at 40 °C of temperature. The potassium uptake in lower doses showed some increase up to 40 °C temperature and in higher doses only up to 20 °C of temperature (Table 12.15).

12.3.5.4 Water Quality

The data summarized in Table 12.16 show the physico–chemical properties of the detergent solution as studied after the growth of *Spirodela polyrrhiza* at varying temperature levels. The turbidity was recorded to be significantly high in 20 ppm and higher detergent concentrations at almost all temperature levels as compared to their corresponding control. The pH of the solutions showed a consistent increase with the concentration level. The pH of the 40 and 50 ppm of the detergent solution was noted to be highest at 40 and 50 °C temperatures. The dissolved oxygen at lower temperature did not show any statistical difference between control and all concentrations of the detergent solution. However, at 20 and 30 °C, the dissolved oxygen significantly reduced in 40 and 50 ppm of Surf Excel as compared to their respective controls. At 40 and 50 °C temperatures the dissolved oxygen was statistically equal ($P > 0.05$) in all detergent concentrations including control. In Surf Excel solutions there were minor reductions in nitrates specifically at 20 and 30 °C. There was no significant difference in the potassium content in all the solutions. However, the phosphate content showed a noticeable difference. The greater phosphate content was recorded in the solutions of higher detergent concentrations. Even 10 ppm of Surf Excel solutions had significantly higher amount of phosphate as compared to control (Table 12.16).

12.3.6 Effect of pH

12.3.6.1 Sensitivity of *Lemna minor*

The data on the growth responses of *Lemna minor* treated at varying pH levels with varying concentrations of Surf Excel detergent are summarized in Table 12.17. The pH and variation in detergent concentration did not affect the dry matter accumulation of *Lemna minor*. Similarly there was no impact on chlorophyll content and potassium uptake but there was a significant increase in nitrogen and phosphorus uptake. The uptake of nitrogen and phosphorus was significantly higher at lower pH and in higher concentrations of Surf Excel. On treatment with 50 ppm of Surf Excel, the optimum nitrogen uptake was recorded at 7.0 pH. The optimum increase in phosphorus uptake was recorded at pH 6.5 and concentration level of 40 and 50 ppm (Table 12.17).

12.3.6.2 Water Quality

Table 12.18 shows the data on physico–chemical properties of the water samples studied after the growth of *Lemna minor* at varying pH and detergent concentrations. The statistical analysis revealed that there was no significant difference in turbidity, DO, nitrates, and potassium contents in water. However, in the detergent solutions there was significantly higher level of phosphates directly related with the concentration levels. But no significant difference in phosphate content was recorded at varying pH and concentration levels of the detergent (Table 12.18).

12.3.6.3 Sensitivity of *Spirodela polyrrhiza*

The data summarized in Table 12.19 shows the growth response of *Spirodela polyrrhiza* grown in varying concentrations of Surf Excel at varying pH levels. The dry matter accumulation was recorded to be higher at acidic pH (6.0–6.5 pH) in almost all detergent concentrations including the control. The chlorophyll contents in *Spirodela polyrrhiza* also increased significantly when treated with higher concentrations of Surf Excel (30–50 ppm) at lower pH (6.0 and 6.5). There was statistically no significant impact of pH on potassium uptake at each concentration levels. The uptake of potassium was, however, observed to be higher in plants grown in 30 and 50 ppm of Surf Excel at all ranges of pH. The uptake of nitrogen was mainly related with the concentrations of detergent. The nitrogen uptake was enhanced with decrease in pH and increase in the concentration level of detergent. The uptake of phosphorus was found related

Table 12.15 Growth response of *Spirodela polyrrhiza* treated in small plastic pots with varying concentrations of Surf Excel at varying temperatures

Parameters	Temp. (°C)	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Dry weight (mg/g)	10	122.80±1.20	124.27±1.23 (+1.2%)	123.97±0.76 (+0.95%)	123.80±2.10 (+0.81%)	126.30±0.87 (+2.85%)	123.32±2.82 (+0.42%)	
	20	126.63±1.15	127.87±1.38 (+0.98%)	128.31±3.20 (+1.33%)	127.93±1.55 (+1.03%)	129.40±1.30 (+2.19%)	127.30±1.37 (+0.52%)	Treatment=0.82
	30	124.70±1.80	126.51±1.16 (+1.45%)	126.77±1.02 (+1.66%)	126.60±1.30 (+1.52%)	132.53±0.75 (+6.28%)	124.73±4.25 (+0.02%)	Temperature=0.75
	40[a]	96.57±2.14	95.53±2.25 (−1.08%)	98.13±3.89 (+1.62%)	98.63±1.27 (+2.13%)	100.27±2.84 (−3.83%)	97.43±1.15 (+0.89%)	Interaction=1.83
	50[b]	80.55±3.15	81.77±1.22 (+1.51%)	81.36±1.12 (+1.01%)	82.35±1.12 (+2.23%)	82.11±1.12 (+1.93%)	82.73±1.86 (+2.71%)	
Chlorophyll-a (mg/g)	10	0.603±0.012	0.644±0.044 (+6.80%)	0.683±0.057 (+13.27%)	0.613±0.058 (+1.66%)	0.655±0.047 (+8.62%)	0.628±0.024 (+4.15%)	
	20	0.575±0.058	0.688±0.060 (+19.65%)	0.770±0.069 (+33.91%)	0.629±0.055 (+9.39%)	0.700±0.038 (+21.74%)	0.620±0.038 (+7.83%)	Treatment=0.007
	30	0.589±0.059	0.672±0.040 (+14.09%)	0.743±0.040 (26.15%)	0.637±0.038 (+8.15%)	0.680±0.038 (+15.45%)	0.647±0.048 (+9.85%)	Temperature=0.007
	40[a]	0.519±0.041	0.536±0.037 (+3.28%)	0.532±0.053 (+2.50%)	0.526±0.047 (+1.35%)	0.528±0.029 (+1.73%)	0.522±0.032 (+0.06%)	Interaction=0.016
	50[b]	0.461±0.061	0.470±0.049 (+1.95%)	0.471±0.021 (+2.17%)	0.468±0.047 (+1.52%)	0.473±0.039 (+2.60%)	0.467±0.054 (+1.30%)	
Chlorophyll-b (mg/g)	10	0.276±0.050	0.299±0.065 (+8.33%)	0.316±0.046 (+14.49%)	0.286±0.062 (+3.62%)	0.286±0.055 (+3.62%)	0.297±0.047 (+7.61%)	
	20	0.275±0.038	0.318±0.035 (+14.91%)	0.299±0.049 (+8.73%)	0.297±0.048 (+8.0%)	0.307±0.039 (+11.64%)	0.307±0.058 (+11.64%)	Treatment=0.007
	30	0.302±0.040	0.382±0.042 (+26.49%)	0.438±0.038 (+45.00%)	0.331±0.048 (+9.60%)	0.383±0.039 (+26.82%)	0.346±0.034 (+14.56%)	Temperature=0.006
	40[a]	0.186±0.051	0.228±0.025 (+22.58%)	0.239±0.038 (+28.49%)	0.188±0.044 (+1.08%)	0.224±0.045 (+20.4%)	0.221±0.010 (+18.82%)	Interaction=0.015
	50[b]	0.211±0.051	0.189±0.050 (−10.43%)	0.192±0.044 (−9.00%)	0.226±0.050 (+7.11%)	0.190±0.030 (−9.95%)	0.542±0.028 (+1.69)	
Total chlorophyll (mg/g)	10	0.883±0.011	0.927±0.104 (+4.98%)	1.191±0.112 (+34.88%)	1.020±0.135 (+15.52%)	1.023±0.110 (+15.85%)	0.906±0.109 (+2.60%)	
	20	0.928±0.129	0.958±0.140 (+3.23%)	1.166±0.109 (+25.65%)	1.047±0.155 (+12.82%)	1.086±0.160 (+17.03%)	0.932±0.110 (+0.43%)	Treatment=0.009
	30	0.903±0.109	0.990±0.095 (+9.63%)	1.222±0.196 (+35.32%)	1.079±0.121 (+19.49%)	1.052±0.153 (+16.50%)	0.868±0.107 (+3.88%)	Temperature=0.008
	40[a]	0.675±0.128	0.691±0.069 (+2.37%)	0.750±0.112 (+11.11%)	0.714±0.069 (+5.78%)	0.723±0.060 (+7.11%)	0.718±0.061 (+6.37%)	Interaction=0.021
	50[b]	0.533±0.133	0.538±0.130 (+0.94%)	0.546±0.041 (+2.43%)	0.556±0.097 (+4.32%)	0.542±0.028 (+1.69%)	0.536±0.027 (+0.56%)	
Nitrogen (mg/100 mg)	10	2.73±0.63	2.85±0.30 (+4.50%)	2.79±0.15 (+2.35%)	2.86±0.20 (+4.76%)	2.75±0.18 (+0.73%)	2.98±0.33 (+9.15%)	
	20	3.18±0.19	3.30±0.46 (+3.90%)	3.29±0.20 (+3.42%)	3.27±0.29 (+2.90%)	3.49±0.29 (+9.74%)	2.60±0.27 (+5.03%)	Treatment=0.17
	30	3.44±0.40	3.60±0.19 (+4.65%)	3.58±0.18 (+4.16%)	3.51±0.51 (+2.03%)	3.78±0.19 (+9.88%)	3.54±0.31 (+2.91%)	Temperature=0.16
	40[a]	2.45±0.29	2.57±0.35 (+4.90%)	2.32±0.30 (−5.31%)	2.52±0.20 (+2.86%)	2.57±0.35 (+4.90%)	2.47±0.29 (+0.82%)	Interaction=0.39
	50[b]	2.14±0.20	2.10±0.29 (−1.87%)	2.06±0.15 (−3.74%)	2.13±0.29 (−0.47%)	2.18±0.19 (+1.87%)	2.10±0.40 (−1.87%)	
Phosphorus (mg/100 mg)	10	0.264±0.059	0.301±0.050 (+14.02%)	0.280±0.012 (+6.06%)	0.283±0.058 (+7.20%)	0.270±0.025 (+2.27%)	0.272±0.057 (+3.03%)	
	20	2.240±0.039	0.282±0.038 (+17.51%)	0.343±0.026 (+42.92%)	0.330±0.028 (+37.50%)	0.291±0.039 (+21.25%)	0.323±0.024 (+34.58%)	Treatment=0.007
	30	0.296±0.061	0.331±0.031 (+11.82%)	0.384±0.029 (+29.73%)	0.371±0.041 (+25.34%)	0.317±0.050 (+7.09%)	0.360±0.040 (+21.62%)	Temperature=0.006
	40[a]	0.276±0.049	0.256±0.050 (−7.24%)	0.272±0.041 (+1.45%)	0.293±0.019 (+6.16%)	0.247±0.041 (−10.50%)	0.268±0.045 (−2.90%)	Interaction=0.016
	50[b]	0.214±0.050	0.219±0.070 (+2.34%)	0.229±0.035 (+7.01%)	0.263±0.041 (+10.28%)	0.216±0.060 (+0.93%)	0.216±0.020 (+0.93%)	
Potassium (mg/100 mg)	10	1.47±0.22	1.50±0.16 (+2.04%)	1.57±0.31 (+6.80%)	1.71±0.76 (+16.33%)	1.59±0.10 (+8.16%)	1.48±0.21 (+0.08%)	
	20	1.69±0.31	1.73±0.31 (+2.49%)	1.95±0.31 (+15.38%)	2.27±0.22 (+34.32%)	1.91±0.32 (+13.02%)	1.86±0.31 (+10.06%)	Treatment=0.037
	30	1.80±0.11	1.60±0.32 (+11.11%)	2.01±0.11 (+11.66%)	2.14±0.11 (+18.88%)	2.02±0.21 (+12.22%)	1.85±0.36 (+2.78%)	Temperature=0.034
	40[a]	1.33±0.11	1.55±0.19 (+16.54%)	1.39±0.33 (+4.57%)	1.35±0.11 (+1.50%)	1.12±0.22 (−15.79%)	1.27±0.11 (+4.51%)	Interaction=0.083
	50[b]	1.13±0.31	1.11±0.21 (−1.77%)	1.19±0.21 (+5.31%)	1.16±0.11 (+2.65%)	1.02±0.21 (−9.85%)	1.10±0.21 (−2.65%)	

Mean ± SD, with in parenthesis percent variation over the control

[a] studied in samples collected at 9th day after the death of plants

[b] studied in samples collected at 5th day after the death of plant

Table 12.16 Physico-chemical characteristics of varying concentrations of Surf Excel detergent studied at 11th day after the growth of *Spirodela polyrrhiza* at varying temperature levels

Parameters	Temp. (°C)	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Turbidity (NTU)	10	10±1	11±2 (+10%)	13±2 (+30%)	13±1 (+30%)	14±1 (+40%)	14±1 (+40%)	
	20	10±1	12±2 (+20%)	14±3 (+40%)	15±2 (+50%)	16±2 (+60%)	17±2 (+70%)	Treatment = 1.2
	30	12±2	13±2 (+8.3%)	15±2 (+25%)	16±2 (+25%)	18±2 (+50%)	19±2 (+58.3%)	Temperature = 1.1
	40[a]	11±2	13±1 (+18.18%)	16±2 (+45.45%)	16±1 (+45.45%)	18±2 (+63.63%)	19±2 (+72.73%)	Interaction = NS
	50[b]	12±1	14±1 (+16.67%)	17±1 (+41.67%)	18±3 (+50%)	19±3 (+58.3%)	20±3 (+66.67%)	
pH	10	7.5±0.4	7.6±0.5 (+1.33%)	7.8±0.4 (+4.0%)	8.1±0.3 (+8.0%)	8.3±0.2 (+10.67%)	8.5±0.1 (+13.33%)	
	20	7.7±0.3	7.8±0.3 (+1.29%)	8.0±0.2 (+3.90%)	8.2±0.5 (+6.49%)	8.4±0.4 (+9.09%)	8.6±0.2 (+11.69%)	Treatment = 0.11
	30	7.5±0.4	7.6±0.2 (+1.33%)	7.7±0.2 (+2.67%)	7.9±0.2 (+5.33%)	8.2±0.2 (+9.33%)	8.4±0.5 (+12.0%)	Temperature = 0.10
	40[a]	7.6±0.3	7.8±0.2 (+2.63%)	8.1±0.4 (+6.58%)	8.3±0.2 (+9.21%)	8.5±0.2 (+11.84%)	8.6±0.2 (+13.16%)	Interaction = 0.25
	50[b]	7.4±0.4	7.5±0.5 (+1.35%)	7.6±0.3 (+2.70%)	7.9±0.3 (+6.76%)	8.2±0.3 (+10.81%)	8.5±0.2 (+14.86%)	
Dissolved oxygen (mg L^{-1})	10	6.6±0.3	6.5±0.3 (−1.52%)	6.4±0.3 (−3.03%)	6.4±0.3 (−3.03%)	6.2±0.2 (−6.06%)	6.0±0.2 (−9.09%)	
	20	6.7±0.3	6.5±0.3 (−2.48%)	6.4±0.1 (−4.48%)	6.0±0.4 (−10.45%)	5.8±0.2 (−13.43%)	5.5±0.2 (−17.91%)	Treatment = 0.09
	30	6.8±0.2	6.3±0.1 (−7.35%)	6.5±0.2 (−4.41%)	5.5±0.4 (−19.12%)	5.3±0.1 (−22.05%)	5.0±0.1 (−26.47%)	Temperature = 0.08
	40[a]	7.0±0.3	6.9±0.4 (−1.43%)	6.8±0.3 (−2.86%)	6.9±0.1 (−1.43%)	6.7±0.2 (−4.29%)	6.6±0.2 (−5.71%)	Interaction = 0.19
	50[b]	7.2±0.3	7.1±0.3 (−1.39%)	7.09±0.2 (−1.49%)	7±0.1 (−2.78%)	6.81±0.2 (−5.56%)	6.7±0.3 (−6.94%)	
Nitrates (mg L^{-1})	10	0.709±0.110	0.706±0.105 (−0.42%)	0.701±0.094 (−1.13%)	0.707±0.101 (−0.28%)	0.702±0.108 (−0.99%)	0.704±0.108 (−0.71%)	
	20	0.690±0.09	0.646±0.047 (−6.38%)	0.622±0.091 (−9.86%)	0.680±0.090 (−1.45%)	0.671±0.110 (−2.75%)	0.675±0.068 (−2.17%)	Treatment = 0.017
	30	0.671±0.110	0.595±0.095 (−11.32%)	0.661±0.089 (−1.49%)	0.696±0.092 (−3.73%)	0.601±0.042 (−10.43%)	0.633±0.083 (−5.66%)	Temperature = 0.017
	40[a]	0.698±0.115	0.677±0.091 (−4.41%)	0.688±0.093 (−1.43%)	0.665±0.075 (−4.73%)	0.687±0.101 (−1.58%)	0.682±0.090 (−2.29%)	Interaction = 0.036
	50[b]	0.713±0.114	0.698±0.092 (−2.10%)	0.708±0.107 (−0.70%)	0.703±0.091 (−1.37%)	0.702±0.109 (−1.54%)	0.700±0.105 (−1.82%)	
Phosphates (mg L^{-1})	10	0.590±0.110	1.065±0.092 (+80.51%)	1.414±0.095 (+139.66%)	1.746±0.163 (+195.93%)	2.064±0.210 (+249.83%)	2.328±0.093 (+294.58%)	
	20	0.600±0.109	1.068±0.190 (+78%)	1.358±0.112 (+126.33%)	1.708±0.144 (+184.67%)	1.991±0.110 (+281.83%)	2.319±0.110 (+286.50%)	Treatment = 0.007
	30	0.570±0.107	1.028±0.485 (+30.35%)	1.381±0.088 (+142.28%)	1.677±0.146 (+194.21%)	2.019±0.191 (+253.86%)	2.256±0.205 (+295.79%)	Temperature = 0.007
	40[a]	0.600±0.106	1.052±0.205 (+75.33%)	1.387±0.208 (+131.17%)	1.727±0.192 (+187.83%)	2.037±0.192 (+239.50%)	2.300±0.196 (+283.33%)	Interaction = 0.017
	50[b]	0.580±0.080	1.041±0.11 (+79.48%)	1.416±0.195 (+144.14%)	1.755±0.103 (+202.59%)	2.053±0.194 (+253.97%)	2.285±0.208 (+293.97%)	
Potassium (mg L^{-1})	10	13.43±2.01	13.30±1.01 (−0.97%)	13.41±1.01 (−0.15%)	13.40±1.00 (−0.22%)	13.35±2.00 (−0.60%)	13.10±0.99 (−2.46%)	
	20	13.40±1.00	13.28±1.99 (−0.90%)	13.35±1.00 (−0.37%)	13.21±0.99 (−1.42%)	13.32±2.11 (−0.60%)	13.04±1.02 (−2.69%)	Treatment = NS
	30	13.36±1.00	13.24±2.0 (−0.90%)	13.32±1.01 (−0.30%)	13.16±1.00 (−1.50%)	13.33±0.99 (−0.22%)	13.05±2.53 (−2.32%)	Temperature = NS
	40[a]	13.42±0.99	13.32±1.01 (−0.75%)	13.42±2.00 (+0.00%)	13.31±2.01 (−0.82%)	13.29±1.99 (−0.97%)	13.09±0.99 (−2.38%)	Interaction = NS
	50[b]	13.43±1.01	13.31±2.01 (−0.89%)	13.42±2.00 (−0.07%)	13.31±1.99 (−0.89%)	13.34±1.0 (−0.67%)	13.12±2.01 (−2.31%)	

Mean ± SD, with in parenthesis percent variation over the control

[a] studied in samples collected at 9th day after the death of plants

[b] studied in samples collected at 5th day after the death of plants

Table 12.17 Growth response of *Lemna minor* treated in small plastic pots with varying concentrations of Surf Excel at varying pH levels

Parameters	pH	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Dry weight (mg/g)	8.0	117.6±2.7	120.3±2.2 (+2.30%)	121.9±3.6 (+3.66%)	129.3±2.8 (+9.94%)	132.0±1.8 (+12.24%)	129.9±3.92 (+10.46%)	
	7.5	116.2±2.6	121.4±1.6 (+4.48%)	123.5±2.6 (+6.28%)	127.9±4.0 (+10.07%)	130.5±4.1 (+12.31%)	131.2±5.6 (+12.91%)	Treatment = 9.18
	7.0	119.8±4.2	122.3±2.2 (+2.09%)	127.3±2.3 (+6.26%)	134.8±1.8 (+12.52%)	128.7±1.8 (+7.43%)	132.8±3.0 (+10.85%)	pH = NS
	6.5	118.7±2.7	125.4±1.5 (+5.64%)	129.3±1.3 (+8.93%)	132.9±5.3 (+11.96%)	136.7±2.0 (+15.16%)	137.5±2.8 (+15.84%)	Interaction = NS
	6.0	119.8±4.1	123.6±2.9 (+3.60%)	125.3±2.5 (+5.03%)	131.1±3.2 (+9.89%)	134.7±4.1 (+12.91%)	131.5±2.7 (+10.23%)	
Chlorophyll-a (mg/g)	8.0	0.564±0.070	0.618±0.073 (+9.57%)	0.641±0.078 (+13.65%)	0.725±0.045 (+28.65%)	0.726±0.099 (+28.72%)	0.707±0.077 (+25.35%)	
	7.5	0.589±0.018	0.603±0.088 (+2.38%)	0.652±0.154 (+10.70%)	0.738±0.030 (+25.30%)	0.743±0.063 (+26.15%)	0.710±0.086 (+20.54%)	Treatment = 0.060
	7.0	0.577±0.054	0.618±0.082 (7.11%)	0.666±0.070 (+15.42%)	0.762±0.081 (+32.06%)	0.730±0.050 (+26.52%)	0.770±0.053 (+33.45%)	pH = NS
	6.5	0.629±0.053	0.692±0.080 (10.02%)	0.683±0.082 (+8.59%)	0.754±0.109 (+19.89%)	0.764±0.076 (+21.46%)	0.788±0.074 (+23.69%)	Interaction = NS
	6.0	0.594±0.095	0.607±0.106 (+2.19%)	0.671±0.083 (+12.96%)	0.772±0.068 (+29.97%)	0.700±0.051 (+17.85%)	0.753±0.084 (+26.77%)	
Chlorophyll-b (mg/g)	8.0	0.260±0.028	0.301±0.015 (+15.77%)	0.291±0.032 (+11.92%)	0.346±0.048 (+33.08%)	0.352±0.038 (+35.38%)	0.360±0.045 (+38.46%)	
	7.5	0.277±0.016	0.311±0.036 (+12.27%)	0.301±0.064 (+8.66%)	0.365±0.053 (+31.77%)	0.325±0.047 (+17.33%)	0.384±0.033 (+38.63%)	Treatment = 0.031
	7.0	0.317±0.024	0.364±0.017 (+14.83%)	0.344±0.077 (+8.52%)	0.399±0.052 (+25.87%)	0.360±0.049 (+13.56%)	0.373±0.038 (+17.67%)	pH = NS
	6.5	0.330±0.029	0.376±0.023 (13.94%)	0.344±0.049 (+4.24%)	0.381±0.043 (+15.45%)	0.452±0.097 (+36.96%)	0.404±0.042 (+22.42%)	Interaction = NS
	6.0	0.278±0.023	0.316±0.023 (+13.67%)	0.325±0.055 (+16.91%)	0.368±0.029 (+32.37%)	0.392±0.033 (+41.0%)	0.386±0.047 (+38.84)	
Total chlorophyll (mg/g)	8.0	0.874±0.123	0.915±0.055 (+4.69%)	1.002±0.143 (+14.65%)	1.195±0.224 (+36.73%)	1.148±0.138 (+31.35%)	1.182±0.115 (+35.24%)	
	7.5	0.887±0.093	0.940±0.102 (+4.69%)	1.048±0.093 (+18.15%)	1.168±0.222 (+31.68%)	1.192±0.176 (+34.39%)	1.209±0.136 (+36.30%)	Treatment = 0.105
	7.0	0.897±0.097	0.962±0.152 (+7.25%)	1.021±0.116 (+13.82%)	1.204±0.178 (+34.23%)	1.157±0.176 (+28.99%)	1.193±0.134 (+33.00%)	pH = NS
	6.5	0.978±0.059	1.057±0.163 (+8.08%)	1.012±0.049 (+3.48%)	1.205±0.130 (+23.11%)	1.204±0.11 (+23.11%)	1.233±0.154 (+26.07%)	Interaction = NS
	6.0	0.965±0.087	0.910±0.081 (+5.70%)	1.026±0.081 (+6.32%)	1.173±0.164 (+21.55%)	1.213±0.205 (+25.70%)	1.239±0.159 (+28.39%)	
Nitrogen (mg/100mg)	8.0	2.87±0.09	3.08±0.52 (+7.46%)	3.71±0.25 (+29.49%)	3.53±0.32 (+23.08%)	3.18±0.36 (+10.74%)	3.73±0.18 (+29.99%)	
	7.5	2.88±0.43	3.13±0.24 (+8.68%)	3.70±0.37 (+28.52%)	3.36±0.35 (+16.57%)	3.62±0.48 (+25.88%)	3.83±0.19 (+32.96%)	Treatment = 0.24
	7.0	2.99±0.27	3.44±0.24 (+14.99%)	3.72±0.25 (+24.50%)	3.05±0.32 (+2.14%)	3.82±0.23 (+27.98%)	4.13±0.28 (+38.15%)	pH = 0.21
	6.5	3.10±0.42	3.73±0.24 (+20.27%)	3.78±0.52 (+22.01%)	3.21±0.47 (+3.68%)	3.95±0.34 (+27.43%)	4.00±0.16 (+29.24%)	Interaction = 0.53
	6.0	3.04±0.20	3.30±0.10 (+8.72%)	3.90±0.21 (+28.37%)	3.42±0.24 (+12.44%)	4.01±0.13 (+31.93%)	3.95±0.31 (+29.95%)	
Phosphorus (mg/100mg)	8.0	0.241±0.034	0.259±0.026 (+7.47%)	0.264±0.083 (+9.96%)	0.336±0.071 (+39.41%)	0.336±0.066 (+39.41%)	0.330±0.058 (+39.93%)	
	7.5	0.269±0.061	0.299±0.054 (+11.15%)	0.272±0.054 (+1.12%)	0.346±0.051 (+28.62%)	0.351±0.065 (+30.48%)	0.371±0.056 (+37.92%)	Treatment = 0.042
	7.0	0.253±0.048	0.273±0.054 (+11.15%)	0.355±0.099 (+40.32%)	0.298±0.074 (+17.79%)	0.338±0.077 (+33.60%)	0.321±0.043 (+26.88%)	pH = 0.038
	6.5	0.299±0.074	0.333±0.077 (+11.37%)	0307±0.054 (+26.76%)	0.382±0.026 (+27.59%)	0.422±0.021 (+41.14%)	0.416±0.035 (+39.13%)	Interaction = NS
	6.0	0.283±0.048	0.360±0.44 (+27.20%)	0.288±0.041 (+1.77%)	0.365±0.053 (+28.98%)	0.369±0.053 (+30.39%)	0.388±0.032 (+37.10%)	
Potassium (mg/100mg)	8.0	1.71±0.34	1.77±0.43 (+3.21%)	2.11±0.31 (+23.42%)	1.82±0.30 (+8.12%)	2.14±0.29 (+24.7%)	2.12±0.45 (+24.01%)	
	7.5	1.71±0.52	1.73±0.36 (+1.41%)	1.99±0.32 (+16.33%)	2.30±0.37 (+34.36%)	2.25±0.29 (+31.79%)	2.24±0.24 (+31.15%)	Treatment = 0.33
	7.0	1.72±0.37	1.73±0.42 (+0.02%)	1.97±0.46 (+14.04%)	2.23±0.29 (+29.29%)	2.28±0.54 (+31.96%)	2.82±0.49 (+32.37%)	pH = NS
	6.5	1.80±0.30	1.87±0.55 (+3.55%)	2.00±0.11 (+11.15%)	2.32±0.19 (+28.58%)	2.30±0.27 (+27.80%)	2.29±0.29 (+27.08%)	Interaction = NS
	6.0	1.78±0.56	1.81±0.43 (+1.35%)	2.02±0.18 (+13.58%)	2.27±0.260 (+27.27%)	2.26±0.37 (+26.99%)	2.25±0.37 (+26.43%)	

Mean ± SD, with in parenthesis percent variation over the control

Table 12.18 Physico–chemical characteristics of water containing varying concentrations of Surf Excel detergent maintained at varying pH levels studied after 11th day of growth of *Lemna minor*

Parameters	pH	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Turbidity (NTU)	8.0	10±1.0	11±0.0 (+11%)	13±2.0 (+30%)	15±1.0 (+50%)	15±2.0 (+50%)	16±3.0 (+60 %)	
	7.5	11±2.0	12±2.0 (+9.09%)	14±3.0 (+27.27%)	15±2.s0 (+36.36%)	16±4.0 (+45.45%)	18±5.0 (+63.63%)	Treatment = NS
	7.0	10±2.0	13±1.0 (+30%)	15±2.0 (+50%)	16±4.0 (+60%)	18±2.0 (+80%)	18±3.0 (+80%)	pH = NS
	6.5	11±3.0	12±2.0 (+9.09%)	13±3.0 (+18.18%)	15±1.0 (+36.36%)	17±1.0 (+54.55%)	18±2.0 (+63.64%)	Interaction = NS
	6.0	11±1.0	12±2.0 (+9.09%)	12±3.0 (+9.09%)	14±4.0 (+27.27%)	15±2.0 (+36.36%)	17±1.0 (+54.55%)	
Dissolved oxygen (mg L^{-1})	8.0	6.9±0.2	6.7±0.2 (−2.90%)	6.3±0.1 (−8.70%)	5.5±0.0 (−20.29%)	5.6±0.4 (−18.84%)	5.4±0.3 (−21.74%)	
	7.5	6.6±0.3	6.2±0.2 (−6.06%)	6.2±0.4 (−6.06%)	5.2±0.4 (−21.21%)	5.3±0.4 (−19.70%)	5.8±0.5 (−12.12%)	Treatment = 0.27
	7.0	6.8±0.5	6.5±0.3 (−4.41%)	6.1±0.6 (−10.29%)	5.7±0.1 (−16.18%)	5.4±0.3 (−20.59%)	5.0±0.4 (−26.47%)	pH = NS
	6.5	6.8±0.2	6.6±0.5 (−2.94%)	6.1±0.6 (−10.29%)	5.5±0.1 (−19.12%)	5.9±0.3 (−13.24%)	5.0±0.3 (−26.47%)	Interaction = NS
	6.0	6.9±0.3	6.9±0.4 (−0.00%)	6.1±0.5 (−11.59%)	5.7±0.4 (−17.39%)	5.6±0.4 (−18.84%)	5.1±0.2 (−26.09%)	
Nitrates (mg L^{-1})	8.0	0.681±0.193	0.610±0.111 (−10.43%)	0.631±0.163 (−7.34%)	0.637±0.056 (−6.46%)	0.535±0.056 (−21.44%)	0.607±0.084 (−10.87%)	
	7.5	0.687±0.191	0.666±0.132 (−3.06%)	0.683±0.174 (−0.58%)	0.599±0.134 (−12.81%)	0.573±0.093 (−16.59%)	0.623±0.078 (−9.32%)	Treatment = 0.202
	7.0	0.643±0.123	0.713±0.145 (−10.89%)	0.572±0.064 (−11.04%)	0.551±0.098 (−14.31%)	0.623±0.050 (−3.11%)	0.570±0.134 (−11.35%)	pH = NS
	6.5	0.603±0.118	0.550±0.116 (−8.79%)	0.529±0.132 (+12.27%)	0.558±0.083 (−7.46%)	0.513±0.038 (−14.93%)	0.541±0.161 (−10.28%)	Interaction = NS
	6.0	0.735±0.160	0.626±0.153 (−14.83%)	0.678±0.145 (−7.76%)	0.586±0.134 (−20.27%)	0.587±0.092 (−20.14%)	0.584±0.147 (−20.34%)	
Phosphates (mg L^{-1})	8.0	0.600±0.111	1.074±0.089 (+79.00%)	1.398±0.233 (+133.00%)	1.717±0.332 (+186.17%)	2.028±0.280 (+238.00%)	2.294±0.319 (+282.33%)	
	7.5	0.620±0.163	1.056±0.161 (+70.32%)	1.354±0.266 (+118.39%)	1.698±0.449 (+173.87%)	2.008±0.140 (+223.87%)	2.275±0.275 (+266.94%)	Treatment = 0.095
	7.0	0.670±0.109	1.029±0.053 (+53.58%)	1.378±0.178 (+105.67%)	1.668±0.280 (+148.96%)	2.065±0.387 (+208.21%)	2.230±0.239 (+232.84%)	pH = NS
	6.5	0.650±0.124	1.011±0.137 (+55.54%)	1.311±0.340 (+115.65%)	1.622±0.317 (+149.54%)	1.957±0.456 (+201.68%)	2.203±0.103 (+238.92%)	Interaction = NS
	6.0	0.620±0.105	0.983±0.251 (+58.55%)	1.337±0.340 (+115.65%)	1.651±0.364 (+166.29%)	1.928±0.369 (+210.97%)	2.246±0.351 (+262.26%)	
Potassium (mg L^{-1})	8.0	13.49±1.51	13.48±1.40 (−0.07%)	13.14±1.25 (−2.59%)	13.37±1.27 (−0.89%)	13.32±1.28 (−1.26%)	13.35±1.39 (−0.96%)	
	7.5	13.46±0.95	13.40±1.54 (−0.45%)	13.34±1.80 (−0.89%)	13.79±1.57 (−2.45%)	13.34±1.38 (−0.66%)	13.29±1.60 (−1.26%)	Treatment = NS
	7.0	13.47±1.42	13.40±1.68 (−0.52%)	13.12±1.00 (−2.60%)	13.25±1.21 (−1.63%)	13.24±1.14 (−1.71%)	13.22±1.11 (−1.86%)	pH = NS
	6.5	13.43±1.23	13.41±0.41 (−0.15%)	13.13±1.23 (−2.23%)	13.31±1.43 (−0.89%)	13.33±1.45 (−0.74%)	13.26±0.76 (−1.27%)	Interaction = NS
	6.0	13.40±1.50	13.36±1.34 (−0.30%)	13.29±1.60 (−0.82%)	13.76±1.28 (−2.69%)	13.24±0.84 (−1.19%)	13.27±1.25 (−0.97%)	

Mean ± SD, within parenthesis percent variation over the control

Table 12.19 Growth response of *Spirodela polyrrhiza* treated in small plastic pots with varying concentrations of Surf Excel at varying pH levels

Parameters	pH	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Dry weight (mg/g)	8.0	122.73±2.17	127.53±2.9 (+3.91%)	132.83±2.16 (+8.23%)	133.53±3.7 (+8.82%)	134.63±2.15 (+9.70%)	125.53±4.08 (+2.12%)	
	7.5	123.93±3.19	126.93±4.2 (+2.42%)	133.23±3.17 (+7.50%)	134.83±2.17 (+8.80%)	135.20±2.91 (+9.44%)	127.42±4.07 (+2.82%)	Treatment = 0.12
	7.0	124.53±4.16	129.83±3.13 (+4.26%)	136.73±0.85 (+9.80%)	134.33±1.86 (+7.87%)	138.13±4.84 (+10.92%)	125.03±1.16 (+0.40%)	pH = 0.11
	6.5	127.53±0.96	128.33±1.84 (+0.63%)	135.33±1.15 (+6.12%)	137.03±7.35 (+7.45%)	135.53±3.17 (+6.27%)	128.23±3.07 (+0.55%)	Interaction = 0.27
	6.0	126.40±1.19	131.53±1.12 (+4.06%)	134.03±3.86 (+6.04%)	138.53±0.84 (+9.60%)	139.42±1.4 (+10.30%)	128.53±1.14 (+1.69%)	
Chlorophyll-a (mg/g)	8.0	0.639±0.057	0.643±0.044 (+0.63%)	0.670±0.071 (+4.85%)	0.743±0.044 (+16.28%)	0.759±0.059 (+18.78%)	0.789±0.059 (+23.47%)	
	7.5	0.658±0.025	0.687±0.069 (+4.41%)	0.693±0.074 (+5.32%)	0.733±0.034 (+11.40%)	0.788±0.049 (+18.23%)	0.770±0.054 (+17.02%)	Treatment = 0.026
	7.0	0.677±0.048	0.738±0.038 (+9.01%)	0.688±0.058 (+1.62%)	0.770±0.042 (+13.73%)	0.809±0.039 (+19.50%)	0.795±0.069 (+17.43%)	pH = 0.026
	6.5	0.626±0.033	0.643±0.021 (+2.72%)	0.677±0.048 (+8.15%)	0.817±0.039 (+30.51%)	0.776±0.049 (+23.96%)	0.816±0.059 (+30.35%)	Interaction = 0.054
	6.0	0.603±0.047	0.647±0.048 (+7.30%)	0.703±0.027 (+16.58%)	0.789±0.021 (+30.84%)	0.803±0.039 (+33.17%)	0.826±0.044 (+36.98%)	
Chlorophyll-b (mg/g)	8.0	0.325±0.039	0.337±0.032 (+3.69%)	0.380±0.059 (+16.92%)	0.421±0.042 (+29.54%)	0.441±0.036 (+35.69%)	0.452±0.035 (+39.08%)	
	7.5	0.327±0.039	0.333±0.021 (+1.83%)	0.386±0.038 (+18.04%)	0.429±0.37 (+31.19%)	0.459±0.038 (+40.37%)	0.450±0.037 (+37.61%)	Treatment = 0.026
	7.0	0.336±0.040	0.348±0.041 (+3.57%)	0.402±0.039 (+19.64%)	0.446±0.045 (+32.74%)	0.462±0.042 (+37.50%)	0.476±0.039 (+41.67%)	pH = 0.026
	6.5	0.333±0.036	0.363±0.039 (+9.0%)	0.397±0.029 (+19.22%)	0.441±0.029 (+32.43%)	0.470±0.059 (+41.14%)	0.467±0.033 (+38.80%)	Interaction = 0.054
	6.0	0.341±0.038	0.352±0.023 (+3.22%)	0.413±0.043 (+21.11%)	0.457±0.028 (+34.02%)	0.478±0.028 (+40.18%)	0.487±0.032 (+42.80%)	
Total chlorophyll (mg/g)	8.0	0.959±0.065	0.993±0.061 (+3.55%)	1.087±0.024 (+13.35%)	1.224±0.067 (+27.63%)	1.261±0.103 (+31.49%)	1.279±0.103 (+33.37%)	
	7.5	0.964±0.120	0.997±0.089 (+3.42%)	1.081±0.053 (+12.14%)	1.230±0.101 (+27.59%)	1.285±0.056 (+33.30%)	1.267±0.074 (+31.43%)	Treatment = 0.075
	7.0	0.977±0.098	1.020±0.092 (+4.40%)	1.092±0.075 (+11.77%)	1.239±0.126 (+26.82%)	1.276±0.038 (+30.60%)	1.298±0.101 (+32.85%)	pH = NS
	6.5	0.973±0.129	1.036±0.099 (+6.47%)	1.098±0.064 (+12.85%)	1.252±0.109 (+28.67%)	1.272±0.019 (+30.73%)	1.302±0.052 (+33.81%)	Interaction = NS
	6.0	0.987±0.084	1.021±0.074 (+3.44%)	1.109±0.024 (+12.36%)	1.242±0.085 (+25.84%)	1.297±0.051 (+31.41%)	1.282±0.049 (+29.89%)	
Nitrogen (mg/100 mg)	8.0	2.96±0.08	3.22±0.09 (+8.78%)	3.82±0.081 (+29.05%)	3.47±0.095 (+17.23%)	3.99±0.070 (+34.79%)	4.01±0.046 (+35.47%)	
	7.5	2.93±0.06	3.18±0.04 (+8.64%)	3.88±0.094 (+32.56%)	3.52±0.085 (+20.26%)	3.91±0.090 (+33.58%)	4.21±0.051 (+43.83%)	Treatment = 0.065
	7.0	3.07±0.19	3.33±0.10 (+8.47%)	3.98±0.081 (+29.64%)	4.04±0.081 (+31.59%)	4.14±0.081 (+34.85%)	4.10±0.064 (+33.55%)	pH = 0.059
	6.5	3.16±0.09	3.47±0.042 (+9.81%)	3.99±0.081 (+26.27%)	3.68±0.070 (+16.45%)	4.26±0.061 (+34.81%)	4.10±0.063 (+29.75%)	Interaction = NS
	6.0	3.13±0.14	3.37±0.09 (+7.77%)	4.15±0.085 (+32.72%)	3.63±0.88 (+16.09%)	4.25±0.056 (+35.91%)	4.37±0.051 (+39.75%)	
Phosphorus (mg/100 mg)	8.0	0.298±0.049	0.333±0.028 (+11.74%)	0.312±0.019 (+4.70%)	0.386±0.015 (+29.53%)	0.363±0.033 (+21.81%)	0.372±0.025 (+24.83%)	
	7.5	0.300±0.058	0.363±0.033 (+21.00%)	0.333±0.029 (+11.67%)	0.406±0.018 (+35.33%)	0.378±0.0150 (+26.0%)	0.377±0.021 (+25.67%)	Treatment = 0.017
	7.0	0.316±0.039	0.347±0.028 (+9.81%)	0.325±0.028 (+2.85%)	0.396±0.012 (+19.62%)	0.417±0.027 (+31.96%)	0.386±0.022 (+25.32%)	pH = 0.016
	6.5	0.310±0.068	0.338±0.063 (+9.03%)	0.316±0.029 (+1.94%)	0.391±0.025 (+25.81%)	0.384±0.016 (+23.87%)	0.393±0.018 (+26.77%)	Interaction = 0.035
	6.0	0.306±0.038	0.352±0.011 (+15.03%)	0.338±0.013 (+10.46%)	0.405±0.014 (+32.35%)	0.368±0.024 (+20.26%)	0.400±0.020 (+30.72%)	
Potassium (mg/100 mg)	8.0	1.87±0.04	2.04±0.10 (+4.32%)	1.95±0.21 (+3.74%)	2.28±0.31 (+21.61%)	2.03±0.21 (+8.27%)	2.05±0.31 (+9.61%)	
	7.5	1.87±0.11	2.04±0.33 (+8.80%)	1.94±0.42 (+3.58%)	2.76±0.31 (+21.45%)	2.02±0.34 (+8.00%)	1.94±0.32 (+3.89%)	Treatment = 0.29
	7.0	1.88±0.20	1.89±0.20 (+0.59%)	1.93±0.21 (+2.88%)	2.28±0.33 (+21.26%)	2.05±0.25 (+9.75%)	1.90±0.39 (+1.17%)	pH = NS
	6.5	1.87±0.21	1.88±0.30 (+0.96%)	2.03±0.31 (+8.94%)	2.04±0.31 (+8.90%)	2.05±0.32 (+9.70%)	2.02±0.21 (+8.03%)	Interaction = NS
	6.0	1.89±0.32	2.09±0.14 (+10.83%)	2.02±0.21 (+6.81%)	2.31±0.38 (+22.13%)	2.06±0.31 (+8.98%)	2.10±0.26 (+10.78%)	

Mean ± SD, within parenthesis percent variation over the control

specifically with the detergent concentration rather than pH. The significant uptake of phosphorus in *Spirodela polyrrhiza* was recorded in 30, 40, and 50 ppm detergent solution at almost all pH levels ranging from 6.0 to 8.0 (Table 12.19).

12.3.6.4 Water Quality

Table 12.20 comprises the data on the physico–chemical characteristics of water with varying concentrations of Surf Excel analyzed after the growth of *Spirodela polyrrhiza*. A glance on the data shows that the turbidity was higher in the solutions of acidic pH 6.0 than in the solution of alkaline pH 8.0. The turbidity was also found to be higher in the detergent solution of 40 and 50 ppm concentration. The turbidity of the detergent solutions at all pH levels was higher. The dissolved oxygen consistently decreased with the increase in the concentration of Surf Excel at all pH levels. The dissolved oxygen at lower pH showed a significant reduction even at lower concentration of the detergent. The nitrate content was highest in control at neutral pH. The nitrates at pH 8.0 did not show much variation at 10 ppm concentration. But at higher concentration (50 ppm), the nitrate contents were lower at pH 6.5–7.5 than in control (probably owing to greater uptake). The phosphates were more significantly related with the concentration of Surf Excel and not with the pH. The potassium contents were slightly lower in Surf Excel solutions as compared to control probably owing to higher uptake of potassium (Table 12.20).

12.4 Discussion

In the screening experiments with 36 selected detergents it was recorded that the dry weight of both the selected duckweeds increased in response to varying detergent concentrations. The growth, (in the form of dry weight) varied with the detergent types and its concentrations. There were three general types of growth pattern. The variation in the type of growth response may be owing to the variations in the relative proportion of constituents of the detergents. There might have been some variation in the relative proportion of the phosphorus content as well. It is evident from the experiments with varying concentrations of Surf Excel (conducted in the polyvinyl and earthen pots) that enough phosphorus was available in the water even after the adequate uptake. Thus, the variation in phosphorus content alone may have not caused variation in responses of the duckweeds to the selected detergents. The detergents used in the present study might have caused varying degree of changes in the water quality parameters.

Some of the factors which affects the growth and development of the aquatic plants include turbidity, temperature, nutrients, dissolved oxygen, CO_2, light, and pH. Shen Dong Sheng and Shen (2002) noted that light intensity, temperature, and nutrients (mainly phosphorus and nitrogen) influenced the algal population in the river network of Zhejiang, China. The phosphorus was considered to be the major determinant in regulating the algal biomass (Shen Dong Sheng and Shen 2002, Kwang-Guk et al. 2003). All the 36 detergents studied might have resulted into the three major sets of aquatic environments with their specific growth responses (Tables 12.5, 12.6, 12.7 and 12.8).

The Surf Excel (a commonly used detergent in India) was selected for the detailed studies on the responses of two selected weeds. Both the duckweeds (in screening experiment) showed type-B growth pattern in response to Surf Excel. The optimum growth of both the duckweeds was observed at 30 ppm of Surf Excel. The duckweeds were studied for their growth responses in large 15 L earthen pots and 150 mL polyvinyl pots to work out the impact of space and volume of the medium. The aquatic microcosm systems have been evaluated as a tool for the quantitative description of phytoplankton, bacteria their nutrient relationship and nutrient cycling in the eutrophication studies (Tsirtsis and Karydis 1997).

In the screening experiments with 36 detergents, three concentrations of the selected detergents (viz., 10, 30, and 50 ppm) were used to study the growth responses of the selected duckweeds. However, in the earthen pot experiment, five concentration levels (10, 20, 30, 40, and 50 ppm) of Surf Excel were used. In the later experiment, the peak of growth of *Lemna minor* was observed at 40 ppm level of Surf Excel. The Surf Excel concentration level up to 50 ppm increased the dry weight accumulation and uptake of phosphorus and nitrogen in *Lemna minor*. The chlorophyll content in *Lemna minor* increased only at lower concentrations (Table 12.9).

The varying concentration of Surf Excel changed the water quality in proportion to their concentration as evident from the data summarized in Table 12.10. The pH, turbidity, and dissolved oxygen varied noticeably with the detergent concentration. The higher pH in the present study retarded the growth of *Lemna minor* and *Spirodela polyrrhiza* (Tables 12.10 and 12.12). It is evident that in addition to phosphate availability, the water quality played more effective role in enhancing the growth of the plants. As evident from the data (Table 12.10), 50 ppm of Surf Excel detergent at lower pH were significantly more effective in promoting the growth of *Lemna minor* as compared to higher pH. The water quality analysis of earthen pots showed 8.8 ± 0.2 pH at 50 ppm of Surf Excel (Table 12.10).

The availability of ions to plant roots has been found to be profoundly affected by hydrogen ion concentration. The monovalent phosphate ion ($H_2PO_4^-$) formed at acidic pH becomes more readily available to the plants. When the medium approaches towards a more alkaline environment, first the production of bivalent phosphate (HPO_4^{2-}) and thereafter the trivalent phosphate (PO_4^{3-}) ions is favored. The biva-

Table 12.20 Physico–chemical characteristics of water containing varying concentrations of Surf Excel detergent maintained at varying pH levels studied after 11th day of growth of *Spirodela polyrrhiza*

Parameters	pH	Concentration (ppm)						LSD at 5%
		0	10	20	30	40	50	
Turbidity (NTU)	8.0	11±1	12±2 (+9.09%)	13±1 (+18.18%)	15±3 (+36.36%)	15±2 (+36.36%)	16±3 (+45.45%)	
	7.5	12±1	13±1 (+8.33%)	14±2 (+16.67%)	16±2 (+33.33%)	17±2 (+41.67%)	18±3 (+50%)	Treatment = 1.13
	7.0	12±1	14±2 (+16.67%)	14±3 (+16.67%)	15±1 (+25%)	16±2 (+33.33%)	17±2 (+41.67%)	pH = 1.03
	6.5	12±1	13±1 (+8.33%)	15±1 (+25%)	16±2 (+33.33%)	18±1 (+50%)	18±1 (+50%)	Interaction = NS
	6.0	12±2	14±1 (+16.67%)	14±2 (+16.67%)	15±3 (+25%)	17±2 (+41.67%)	19±3 (+58.33%)	
Dissolved oxygen (mg L^{-1})	8.0	6.81±0.65	6.66±0.19 (−2.20%)	6.15±0.38 (−9.69%)	5.16±0.30 (−24.23%)	5.44±0.31 (−20.11%)	4.93±0.28 (−27.61%)	
	7.5	6.76±0.49	6.62±0.27 (−2.07%)	6.51±0.52 (−3.70%)	5.73±0.30 (−15.24%)	4.93±0.44 (−27.07%)	5.01±0.17 (−25.89%)	Treatment = 0.064
	7.0	6.62±0.54	6.38±0.20 (−3.63%)	6.10±0.50 (−7.85%)	5.16±0.65 (−22.05%)	5.06±0.42 (−23.56%)	4.80±0.45 (−27.79%)	pH = 0.059
	6.5	6.38±0.53	6.03±0.33 (−5.49%)	5.97±0.55 (−6.43%)	5.20±0.66 (−18.50%)	5.22±0.40 (−18.18%)	4.61±0.39 (−27.74%)	Interaction = 0.144
	6.0	6.56±0.52	6.08±0.45 (−7.32%)	6.31±0.32 (−3.81%)	4.79±0.36 (−26.98%)	5.31±0.25 (−19.05%)	4.66±0.59 (−28.96%)	
Nitrates (mg L^{-1})	8.0	0.632±0.045	0.628±0.048 (−0.63%)	0.612±0.080 (−3.13%)	0.605±0.063 (−4.23%)	0.622±0.044 (−1.58%)	0.594±0.048 (−6.01%)	
	7.5	0.644±0.029	0.582±0.044 (−9.63%)	0.639±0.048 (−0.78%)	0.618±0.050 (−4.04%)	0.601±0.051 (−6.68%)	0.555±0.034 (−13.82%)	Treatment = 0.016
	7.0	0.648±0.037	0.631±0.070 (−2.62%)	0.611±0.086 (−5.71%)	0.632±0.065 (−2.47%)	0.605±0.048 (−6.64%)	0.590±0.045 (−8.95%)	pH = 0.015
	6.5	0.626±0.052	0.584±0.056 (−3.71%)	0.581±0.065 (−5.59%)	0.618±0.062 (−1.28%)	0.616±0.076 (−1.60%)	0.571±0.045 (−8.79%)	Interaction = 0.034
	6.0	0.61±0.077	0.598±0.036 (−2.45%)	0.546±0.042 (−10.93%)	0.550±0.077 (−10.28%)	0.590±0.050 (−3.75%)	0.576±0.038 (−6.04%)	
Phosphates (mg L^{-1})	8.0	0.654±0.052	1.026±0.109 (+56.88%)	1.323±0.110 (+102.29%)	1.674±0.201 (+155.96%)	1.986±0.250 (+203.67%)	2.228±0.406 (+240.67%)	
	7.5	0.660±0.061	0.997±0.203 (+51.06%)	1.357±0.092 (+105.60%)	1.646±0.292 (+149.39%)	1.947±0.228 (+195.00%)	2.247±0.392 (+240.45%)	Treatment = 0.095
	7.0	0.668±0.067	1.004±0.113 (+50.29%)	1.326±0.202 (+98.50%)	1.665±0.090 (+149.25%)	1.956±0.085 (+192.81%)	2.254±0.217 (+237.43%)	pH = NS
	6.5	0.640±0.048	10.17±0.192 (+58.90%)	1.309±0.208 (+104.53%)	1.639±0.429 (+156.09%)	1.978±0.321 (+209.06%)	2.204±0.329 (+244.38%)	
	6.0	0.643±0.042	0.979±0.115 (+52.26%)	1.344±0.102 (+109.02%)	1.624±0.332 (+152.27%)	1.926±0.260 (+199.33%)	2.226±0.195 (+246.19%)	
Potassium (mg L^{-1})	8.0	13.24±0.037	12.83±0.052 (−3.09%)	13.16±0.048 (−0.60%)	13.23±0.032 (−0.08%)	13.06±0.029 (−1.36%)	13.14±0.040 (−0.76%)	
	7.5	13.22±0.074	12.81±0.033 (−3.10%)	13.17±0.035 (−0.38%)	13.17±0.049 (−0.38%)	13.00±0.039 (−1.66%)	13.15±0.045 (−0.53%)	Treatment = NS
	7.0	13.43±0.055	13.35±0.070 (−0.60%)	13.11±0.047 (−2.38%)	13.21±0.033 (−1.64%)	13.25±0.026 (−1.34%)	13.31±0.054 (−0.89%)	pH = NS
	6.5	13.45±0.082	13.30±0.059 (−1.11%)	13.20±0.055 (−1.86%)	13.19±0.031 (−1.93%)	13.28±0.052 (−1.26%)	13.33±0.048 (−0.89%)	Interaction = NS
	6.0	13.27±0.038	12.85±0.092 (−3.19%)	13.24±0.041 (−0.23%)	13.16±0.025 (−0.83%)	13.14±0.054 (−0.98%)	13.21±0.050 (−0.45%)	

Mean ± SD, within parenthesis percent variation over the control

lent and trivalent forms of phosphate ions are not as readily available to the plants as monovalent phosphate ions (Devlin and Witham 1986). The data of Table 12.11 suggested that the 40 ppm of the Surf Excel increased the dry weight, chlorophyll content, and uptake of NPK in the *Spirodela polyrrhiza*.

It also emerged from the data that increasing concentration of Surf Excel resulted into a proportional increase in the pH of the water medium. Thus, despite increased availability of phosphate, probably its ionic forms consistently changed from monovalent to bivalent and trivalent ions which proportionally reduced the uptake of NPK in both the duckweeds at 50 ppm as compared to uptake at 40 ppm of Surf Excel (Tables 12.9 and 12.11). Moreover, the cells in the fronds of a *Lemna* species have proton extrusion pump at the plasmalemma which is responsible for the energy-dependent component of the membrane potential (Ansari and Khan 2006b; Novacky et al. 1978a, b; Löppert 1979; Jung and Lüttge 1980). This pump is responsible for the uptake of sugars, amino acids, phosphates, nitrates, and perhaps other inorganic ions by means of H^+-co transport mechanism (Ullrich-Eberius et al. 1978, 1981; Fischer and Lüttge 1980; Böcher et al. 1980; Lüttge et al. 1981).

The findings of the present work also established the ecological importance and sensitivity levels of the *Lemna minor*. Aziz and Mobina (1999) reported that pH 6.0 was most suitable for two species of *Spirodela polyrrhiza* and *Spirodelapunctata*. The *Spirodela polyrrhiza* died at pH 4.0. Both the species of *Spirodela* grew quite well up to pH 9. In both the species low pH affected the chlorophyll *b* formation (Aziz and Mobina 1999). Riis and Sand (1998) found a direct relationship between macrophyte distribution and pH, nutrient conditions, and transparency of Danish lakes.

The phosphorus is an important constituent of ATP, ADP, nucleic acids (DNA and RNA), phospholipids, and proteins. The meiotic cell division in sexual reproduction and mitotic cell division in vegetative propagation require greater supply of phosphorus for its binding into required nucleic acids, phospholipids, and protein. When grown singly, the phosphorus uptake in *Lemna minor* at 40 ppm of Surf Excel was almost 23 % higher than the control (Table 12.9). The phosphorus uptake in *Spirodela polyrrhiza* was 60 % higher (than the control) at 40 ppm of Surf Excel (Table 12.11).The plants have specific controls for the uptake of solutes, whether they have osmotic roles in the cells or the solutes are used as nutrients. The uptake of phosphate depends upon the phosphate status of the plants (Ullrich-Eberius et al. 1981).

A direct relationship between phytoplankton minima and maxima was found related with the DO content by a number of workers (Lande 1973; Misra et al. 1975; Saad 1973; Schindler 1971). As evident from the data of the water quality (Tables 12.10, 12.12) the dissolved oxygen and turbidity of water was impaired to a relatively greater extent by *Spirodela* sp. as compared to *Lemna* sp. Thus, the *Spirodela polyrrhiza* modifies the aquatic environment more actively than the *Lemna minor*. Such modifications in the environment by component species themselves, results into the succession of community to a higher seralstage. Any change in the natural quality of water is best reflected in the change in natural flora and fauna of the aquatic ecosystem (Kulshrestha et al. 1989). The eutrophication reduced the number of rare species and increased the abundance of meso- to hypereutrophic species specifically *Fragilariaberolinensis* in the eutrophic broad area of De NieuwkoopsePlassen in the Netherlands (Van Dam and Mertens 1993).

In the present work, temperature played important role in the growth of both the selected duckweed species. The optimum growth increase was noted at 30 °C temperature. The temperature of 20 and 30 °C increased the uptake of NPK specifically of phosphorus. The higher temperatures adversely affected the chlorophyll content in both the species eventually the excessive chlorosis and necrosis lead to faster duckweed mortality. The nitrogen uptake was optimum in both the species at 30 °C of temperature (Tables 12.15 and 12.17).The chlorophyll concentration was found strongly linked to the total nitrogen concentration. During summer, nitrogen concentrations accounted for about 60 % of the variability in chlorophyll concentration among different coastal systems (Neilson et al. 2002). It appears that higher temperature of 40 and 50 °C impaired the nitrogen availability and thereby reduced the chlorophyll content and thus, caused early disappearance of both the duckweeds by 5th to 9th day from the treatment. The temperature deviations are believed to impose stresses on plants leading to abnormalities resulting into reduced chances of survival (Ansari and Khan 2006b; Treshow 1970).

The temperature regulates cell division rate, enzyme activity (Giese 1979), translocation, and synthesis of food material (Devlin and Witham 1986). The development of plant, metabolic activities, mineral absorption, and water uptake are strongly temperature dependent (Treshow 1970; Devlin and Witham 1986). The lower temperatures below 10 °C (Ghosh et al. 1995) have been reported to retard the growth and productivity of duckweed. The temperature between 20 and 30 °C was found optimum by Hillman (1961). Aziz and Mobina (1999) found 25–33 °C temperature were optimum for the growth of two species of *Spirodela*. The photosynthesis is also dependent upon the enzyme activity which is reported to be negligible below 10 °C and to be optimum at 30 °C in most of the plant species (Treshow 1970). The role of several other parameters (viz. direct impact of detergents on the cell membranes, injuries and leakage of ions out of the fronds cells) in modifying the responses of both duckweeds cannot be ruled out. It is suggested that more detailed studies are needed to have a deeper insight on the physio–morphological responses of the duckweeds.

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Estimating Fish Production in the Itaipu Reservoir (Brazil): The Relationship Between Fish Trophic Guilds, Limnology, and Application of Morphoedaphic Index

13

Rinaldo Antonio Ribeiro Filho, Julia Myriam de Almeida Pereira and Simone Friderigi Benassi

Abstract

Many experimental studies contributed to the development of the theory of the lacustrine food web, disclosing the important paper of the fish, for decades ignored by the limnology. This work is based on the hypothesis of the trophic cascade relations, particularly related to bottom-up and top-down effect in Itaipu Reservoir (Brazil). Using the made data available by Itaipu Binacional, from 1999 to 2004, analyses of multiple regressions were accomplished to determine the relationships of the dependent and independent variables. A negative effect was verified between the water transparency in relation to suspended solids and turbidity. The chlorophyll-a presented positive relationship with total nitrogen. The omnivorous, detritivorous, and insectivorous fishes presented a negative effect (control) in the cyanobacteria concentrations and chlorophyll-a. The estimate of the production of fish in the reservoir was better related with the concentrations of cyanobacterias of the reservoir. The top-down and bottom-up effect had been confirmed, the forces top-down had been found only in the first trophic level, and the others presented bottom-up effect.

Keywords

Trophic cascade reservoir · Limnology · Biotic community · Fish yield

13.1 Introduction

13.1.1 Relationship Between Fish and Water Quality

Fish plays an important role in the biocenosis of reservoirs when it comes to water quality. The presence or absence of certain species, together with the amount of fish in the system helps to determine the composition and quantity of nutrients, zooplankton, and phytoplankton in reservoirs (Straškraba and Tundisi 2000).

The ichthyofauna of a reservoir is altered according to water quality owing to two factors: (a) contamination by pollutants from tributaries, what can affect various parts of the reservoir and (b) changes in how the hydrological system works (Straškraba and Tundisi 2000). The composition of species of the fauna depends largely on geographical characteristics and lakes and reservoirs are characterized by the

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absence of true pelagic species, and most of the reservoirs are populated by species that typically inhabit the coastal region.

13.1.2 Trophic Cascade Interactions in Reservoirs

The trophic cascade theory in lakes and reservoirs is based on two principles: (1) loss of energy between a trophic level and another and (2) disturbance of a trophic level with consequences in the remaining trophic levels.

The pioneer work of Hrbáček et al. (1961) was responsible for highlighting the effect of fish on the structure of the aquatic food chain. After a few years, research such as Brooks and Dodson (1965) and Shapiro et al. (1975) contributed to the development of the food web theory in lakes, revealing the important role of fish, ignored for decades in the field of limnology.

The first book that dealt with the cascade effect in lakes was "*The trophic cascade in lakes*" (Carpenter and Kitchell 1993). In this work the authors discuss topics such as: trophic cascade interactions, fish behavior in response to manipulation, the dynamics of phytoplankton and zooplankton, interaction between primary productivity and nutrients, simulation models of trophic cascade, among others, being of great importance to understanding how trophic cascade effects work in aquatic ecosystems.

The theory of trophic cascades (Carpenter and Kitchell 1993; see critiques from Demelo et al. 1992; and the meta-analyses of Brett and Goldman 1996, 1997) and the bottom-up/top-down theory (Mcqueen et al. 1986) are the two main conceptual models of work used here. Phytoplankton responds positively to nutrient-enriched systems with an odd number of trophic levels (three levels: phytoplankton, zooplankton, and planktivorous fish), but not in systems with an even number of trophic levels (two levels without fishes, or four levels with piscivorous fishes).

The effect of the stock of planktivorous fish on the zooplankton community has been well-studied (Arcifa et al. 1986; Lazzaro 1987; Lazzaro 1991) and there is strong pressure of these fish on the biomass of algae (Pijanowska and Prejs 1997; Jeppesen et al. 1997). The effect of piscivorous fishes in a system has a strong relationship with the stock of planktivorous fishes, causing the drastic reduction of latter (Mcqueen 1990; Demelo et al. 1992; Hambright 1994). Some studies confirm that the impact of fish stocks favors the concentrations of chlorophyll through the excretion of nutrients and the predation of zooplankton (Mcqueen et al. 1992; Lazzaro 1997; Drenner 1998; Starling 1998). With regard to the stock of piscivorous fishes, many studies were not successful (Demello et al. 1992; Mcqueen et al. 1992), mainly owing to the low stocking density (Perrow et al. 1997). In many studies the top-down effect was observed (Shapiro et al. 1975; Shapiro and Wright 1984; Carpenter et al. 1985; Persson et al. 1988; Mcqueen, 1990; Faafeng and Brabrand 1990; Carpenter and Kitchell 1993; Pijanowska and Prejs 1997; Sondergaard et al. 1997; Prejs et al. 1997; Meijer et al. 1999).

Carpenter et al. (1985) suggest that knowing how the food chain works can be useful for the management of aquatic ecosystems aiming at ecology conservation. The increase of piscivorous fishes may decrease the density of planktivorous ones and, consequently, increase grazing and depletions in the concentrations of chlorophyll-a. The increase in the stock of piscivores can be a tool for rehabilitating eutrophic lakes. The concept of trophic cascade with links between limnology and fisheries biology suggests a biological alternative for lake management.

Studies by Brett and Goldman (1996) prove the theory of trophic cascade. They noted that the manipulation of fish communities can be used to control algal biomass, but these relationships are fragile. The authors mention that the control of the phytoplankton through the trophic cascade management (biomanipulation) can be successful in about 60 % of the cases and that the reduction zooplanktivorous species would result in a slight reduction in phytoplankton biomass and hence a small improvement in the quality of water.

Borer et al. (2005) tested the trophic cascade hypothesis using a review of 114 studies with tested indirect trophic relations. The biomass of predators had a direct effect on plant biomass, both in terrestrial and aquatic environments. A combination of herbivory and metabolic and taxonomic factors of predation explained 31 % of the cascade relationships among all 114 studies. Within systems, 18 % of the cascade relationship was explained owing to the predators that have similar characteristics to herbivores. In all systems, the strongest cascades occurred in invertebrate herbivores and endothermic vertebrate predators associations. These associations are derived from a combination of real biological differences among species with different physiological requirements, and the influence of organisms studied in different systems.

Benndorf et al. (2002) mention that the top-down control of chlorophyll-a occurs according to the following conditions: (i) short-term experiments, (ii) shallow lakes with macrophytes and (iii) deep slightly eutrophic or mesotrophic lakes. Other experiments indicate that top-down control may be unlikely in the following conditions: (iv) eutrophic or hypertrophic deep lakes, unless there is severe limitation of light, and (v) for all lakes when there is extreme nutrient limitation (oligotrophic and ultraoligotrophic lakes). Important factors that are responsible for the top-down control under the described conditions in (i) and (iii) are the time scales that prevent the slow development of phytoplankton; shallow depths allow macrophytes to become dominant primary

producers (ii), and biomanipulation-induced reduction of phosphorus (P) available to phytoplankton (iii).

Bell et al. (2003) conducted trophic cascade experiments in experimental ponds over a period of 4 years. The results of this study showed further development of phytoplankton related to the increase of piscivore biomass. The authors stress that most studies, no matter if they are trophic cascade effect experiments or not, are developed in short-term scale. The authors emphasize that the result of experimental manipulations in ecology should depend on the duration of the experiment, and this factor is crucial to test the trophic cascade hypothesis in lakes.

Mehner et al. (2005) compared the data of trophic (limnological) variables with the spatial and temporal distribution of fishes, zooplankton, and phytoplankton. According to the analysis (meta-analysis), the distribution of the studied trophic levels was correlated with the temperature of water and nutrient concentration distributions.

13.1.3 Tropical and Subtropical Trophic Cascades

According to Lazzaro et al. (2003), the dams in the semi-arid northeastern region of Brazil offer excellent opportunities for theoretical comparisons on the relative importance of the top-down and bottom-up impact structuring forces on the fish-plankton interactions in tropical environments, including comparisons between the effects of the dominance of omnivorous and low number of piscivorous species. However, most of the dams have never been studied, except for some large public ponds, especially those controlled by DNOCS—Departamento Nacional de Obras Contra a Seca (National Department of Works Against Droughts) in the states of Ceará and Paraíba. Regional reports on fishery yield, hydrochemistry, and limnology (e.g., Davies 1972; Gesteira 1978; Silva 1981; Wright 1981; DNOCS 1990; Molle 1991; Gurgel and Fernando 1994; Paiva et al. 1994; Bouvy et al. 1998) were rare. The author points out that to make generalizations it is more appropriate to use a comparative approach based on data from climatology, limnology, and plankton communities and fish collected in the reservoir, and studies correlating all these variables are in small number (Regier and Henderson 1980; Quiros 1990). Studies with this type of approach can provide important practical and social implications for predictive limnology (Peters 1986), for the management of fishery yield (Schlesinger and Regier 1982) and/or water quality.

While studying 31 Argentinian reservoirs, Quirós and Boveri (1999) have shown that in environments in which the effect of piscivorous stock did not cause a depletion of zooplanktivores, the phytoplankton biomass reduced drastically. The authors emphasized that human influence can cause changes in trophic relationships in lakes and reservoirs.

Rejas et al. (2005) evaluated the top-down and bottom-up effects in a floodplain lake in Bolivia. The authors found two types of effects on the trophic cascade in experiments in mesocosms, and the effect of these relationships varied among trophic levels. The effect of planktonic fishes did not show any positive relationship with zooplankton, mainly with cladocerans, and phytoplankton showed bottom-up effect.

The objectives of this work were to evaluate the water quality of the Itaipu Reservoir (central body and arms of the left bank of the reservoir) through the analysis of physical, chemical, and biological variables, given the multiple uses of the reservoir during the period from 1999 to 2004; to analyze the evolution of the trophic levels of the reservoir, including its left margin arms, and characterize the trophic webs and the relationship between the relative fish biomass, plankton, and limnology of the Itaipu reservoir.

13.2 Materials and Methods

13.2.1 Characterization of the Study Area

The Paraná River is the tenth longest river in the world (4,695 km), and was considered the most important hydrological system of the La Plata River Basin (Borghetti et al. 1988). It is formed by the confluence of the rivers Grande and Parnaíba (center-south of Brazil), flowing into La Plata River, north of Argentina (Agostinho and Gomes 2005). The Paraná River Basin is responsible for more than 70% of hydroelectric power production in Brazil, has the largest population density in South America and includes other major rivers, such as the rivers Grande, Tietê, Parnaíba, Paranapanema, and Iguaçu, were approximately 130 dams were constructed (Fig. 13.1).

The Itaipu Reservoir, completed in October 1982, is located in the Brazil-Paraguay border, between latitudes 24º05'S and 25º33'S and between longitudes 54º00'W and 54º37'W (Grw). It has a surface of 1,350 km^2 in its mean elevation of operation (220 m) and 1,460 km^2 when in maximum height (223 m). Of these, 625 km^2 are part of Brazil and 835 km^2 of Paraguay. It stretches over 151 km (170 km in maximum quote) and separates the cities of Guairá—Salto del Guayra and also Foz do Iguaçu—Ciudad del Este (Agostinho et al. 1999).

With an average depth of 22 m, and possible depths of 170 m near the dam, the Itaipu reservoir accumulates as normal maximum volume, 29,109 m^3 of water. The residence time in the main channel is 29 days and the speed of the water can reach 0.6 m/s. The average residence time is, however, 40 days. It operates with a maximum annual level variation of 0.6 m (Itaipu Binacional 2006).

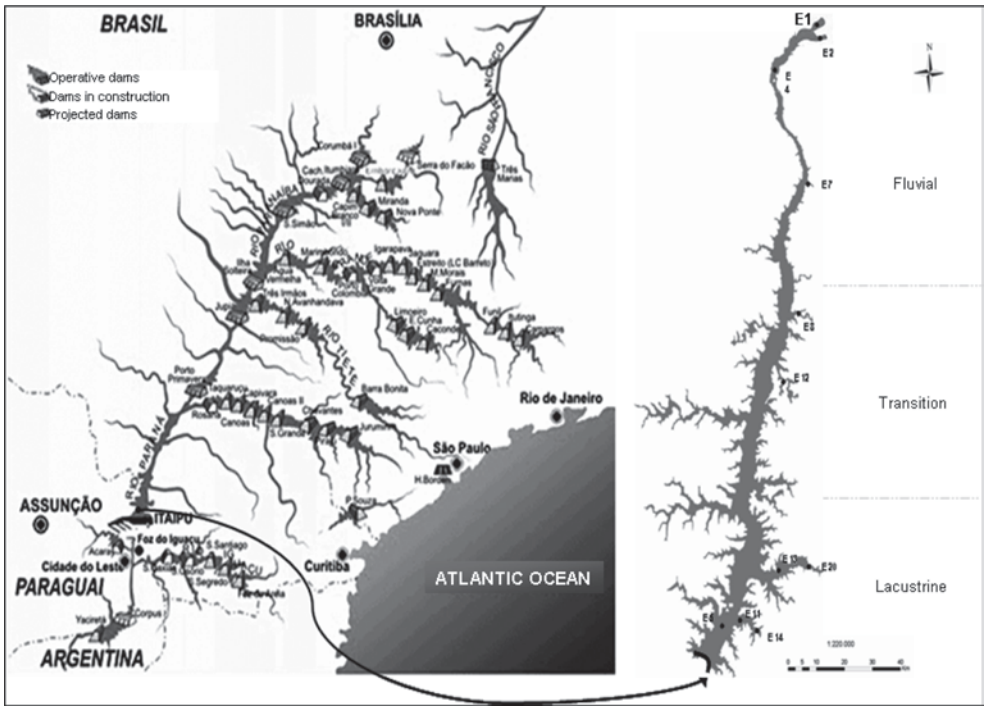

Fig. 13.1 The Paraná River basin, with its reservoirs. (Source: Itaipu Binacional, 2006)

Energy production is the main use of the Itaipu reservoir, which was the primary motivation for its construction. However, other secondary uses are currently coming into scene, especially (i) navigation, facilitated by the drowning of The Sete Quedas Falls (Guaira), (ii) recreation and tourism, mainly in five artificial beaches built on its banks, (iii) water supply for cities and irrigation of smallholdings, and (iv) professional fishing (Agostinho et al. 1997a).

Based on Carlson's trophic state index (phosphorus and chlorophyll-a), this reservoir was classified as mesotrophic, and some eutrophic areas may be found in its arms during certain periods of the year. It presents an annual cycle of thermal stratification in its main body (spring-summer), which classifies it as a monomictic hot lake, besides daily stratification processes in its arms.

The fish assemblage of the Itaipu reservoir and its catchment area is composed of 114 species in all environments. The dominant species vary with the type of environment, because this is a factor that contributes significantly to the structure of this assemblage (annual report Itaipu Binacional).

13.2.2 Characterization of the Sampling Stations

To establish the location of the sampling stations we considered the compartmentalization of the Itaipu Reservoir, which is composed by three horizontal regions, along the main body of the reservoir (Agostinho et al. 1997b; Agostinho et al. 1999; IAP 2003; Oliveira et al. 2005): (1) the riverine zone: located at the beginning of the reservoir, (2) the transition region: between the lotic and lentic regions, and (3) the lentic region, called ''lacustrine region,'' where the reservoir is usually deeper and wider.

Furthermore, the Itaipu Reservoir has a dendritic form, what means that attached to its central body there are branches on the sides called reservoir arms which present systems that are almost independent from the main body system and that have their own particular characteristics. Owing to this compartmentalization, a network of water quality monitors was established, totaling 12 sampling stations (Fig. 13.2).

Stations E1, E2, E3, and E7, in areas of lotic characteristics are in the riverine zone. Stations E5, E11, E12, E14, and E20 are in the lacustrine region and stations E8 and E12 are in the transition region.

13.2.3 Data Collection

The data analyzed in this study were provided by Itaipu Binacional. Limnological analyses, including physical and chemical water variables, phytoplankton, and zooplankton were made by Instituto Ambiental do Paraná (IAP), the Environmental Institute of Paraná, based on quarterly collections, between 1999 and 2004. Information on fish stocks are from the studies conducted by Núcleo de Pesquisa em Limnologia, Ictiologia e Aquicultura (NUPELIA/UEM), the Center for Research in Limnology, Ichthyology and Aquaculture.

According to the IAP (2003), samples were collected at the water surface, and the physical, chemical, and biological water quality variables were monitored in all field samplings. The following variables were measured in the field:

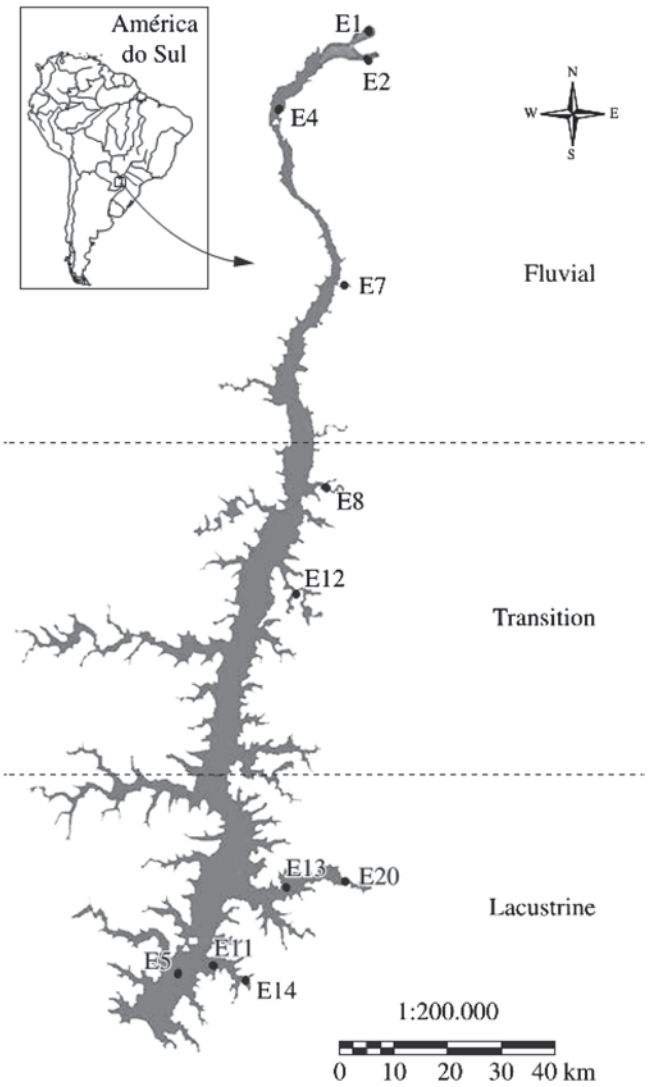

Fig. 13.2 Morphometry and sampling sites in the Itaipu Reservoir, with the riverine, transition, and lacustrine zones adopted in the monitoring program

temperature, dissolved oxygen concentration and percentage of saturation, pH, electrical conductivity, and water transparency. Other physical and chemical variables, such as alkalinity, total nitrogen Kjeldahl (TKN) nitrate, nitrite, ammonia and nitrogen, total solids, suspended solids, BOD, COD, and total phosphorus were analyzed in the laboratory, according to APHA (1985), as well as the concentration of chlorophyll-a (NUSCH, 1980). The analysis protocols were presented by Ribeiro Filho (2005).

The climatological data were obtained from weather stations in the cities of Guaira (riverine area), Entre Rios do Oeste (transition zone), and Iguazu Falls (lacustrine-downstream zone).

Data on fishes were grouped into trophic guilds, according to Oliveira et al. (2005). They presented the relative densities, calculated from numerical abundance in kilograms, corresponding to the weight of gutted fish without a head.

The relative abundance of phytoplankton, zooplankton, and fish were presented according to the regions (riverine, transition, and lacustrine) of the reservoir to enable the comparison of the spatial distribution patterns.

13.2.4 Statistical Analysis of Data

To test the trophic cascade hypothesis in the reservoir,we performed linear regression analyses among the physical, chemical, biological, and trophic guilds, and trophic levels were analyzed one by one, determining the interactions between them. These analyses were performed in accordance with food web models (Top down and Bottom up) (Carpenter et al. 1985; Mcqueen et al. 1986; Lazzaro 1997; Lazzaro et al. 2003). The graphs were evaluated to determine whether the relationships were linear or not. To stabilize the variance, the Neperian logarithms were taken for all limnological variables. Graphically, limnological variables were expressed according to the equation below:

$$\text{In var} = \text{In(var)}$$

where *var* is the original value of the limnological variable; *ln var* is the transformed value of *var*.

For biotic variables, in order to minimize null values, the transformation was performed according to the following equation, based on absolute numerical abundance:

$$\text{In bio} = \text{In(bio} + 1)$$

where *bio* is the original value of the biotic variable + 1, *ln bio* is the transformed value of *bio*.

In the analysis of residues, assumptions of linearity, normality, and homoskedasticity were confirmed.

To test the effect of limnological and fish biomass on chlorophyll-a and cyanobacteria we carried out multiple regression analyses following the *stepwise* procedure, in which all variables were tested, and as they did not produce any significant results, they were one by one discarded from the model.

To test the hypothesis that the chlorophyll-a, and therefore the productivity of the reservoir, depends on the concentration of nutrients, a multiple regression analysis was performed. The concentration of chlorophyll-a was considered a dependent variable, and was plotted with the forms of nutrients (independent variable), and only those that showed significant results remain present in the final model.

In order to detect possible relationships between the biotic and abiotic variables we carried out multiple regression analyses. These used the densities of cyanobacteria, the concentration of total phosphorus and biomass of fishes (omni-

Table 13.1 Results of multiple regression analysis assessing the effect of ammonia nitrogen, TKN, nitrate, and total *P* variables on concentrations of chlorophyll-a in the Itaipu Reservoir, for the period from 1999 to 2004

	Coefficient	Std. error	T	*p*	VIF
Constant	0.743	0.193	3.852	<0.001	
Ammonia nitrogen	−0.308	0.108	2.838	0.005	1.101
TKN	0.755	0.0845	8.940	<0.001	1.150
Nitrate	−0.184	0.095	−1.923	0.056	1.004
P total	0.189	0.0691	2.733	0.007	1.082

vores and detritivores) as dependent variables, what turned out to be of relevance in the linear regression analyses performed. The analyses follow the same protocol of the abiotic variables analyses.

13.2.5 Trophic State Index (TSI)

In order to assess the trophic state of the Itaipu Reservoir, we used the trophic state index proposed by CARLSON and modified by Toledo Jr et al. (1983), as described below:

$$\text{TSI (Secchi)} = 10\left[6 - \left(\frac{0.64 + \ln \text{Secchi}}{\ln 2}\right)\right]$$

$$\text{TSI } (P \text{ Total}) = 10\left[6 - \left(\frac{\ln\{80.32 / P \text{ total}\}}{\ln 2}\right)\right]$$

$$\text{TSI (Chlorophyll)} = 10\left[6 - \left(\frac{2.04 - 0.695 * \ln \text{Chlorophyll-a}}{\ln 2}\right)\right]$$

To determine TSI (mean), the calculation of the index was done using the weighted average by assigning a lower weight to the transparency of water, as suggested by Toledo Jr et al. (1983). Thus, to calculate the TSI (mean), we used the following formula:

$$\text{TSI (Mean)} = \frac{\text{TSI (Secchi)} + 2\left[\begin{matrix}\text{TSI}(P \text{ total}) \\ +\text{TSI(Chlorophyll-a)}\end{matrix}\right]}{5}$$

13.2.6 Estimate of Fishing Yield

Through Morfoedaphic Index (MEI) of RYDER (1965), we estimated fishing yield and the MEI was expressed by the following equation:

$$\text{MEI} = \frac{\text{TDS}}{\text{zm}} \text{ or } \text{MEI} = \frac{\text{conductivity}}{\text{zm}}$$

Where TDS = concentration of dissolved solids (mg/L) and zm = average depth (m).

13.2.7 Inference of Fishing Yield

In order to estimate the fishing yield of the Itaipu reservoir and verify if the predicted index values were significant we used the equation proposed by Meleck (1976), with the model derived from a capture data regression analysis and MEI (morfoedaphic index):

$$\text{FY} = 4.1 \times \text{MEI}^{0.8}$$

The index below (MEI) is a relationship between the concentrations of dissolved solids in water divided by the mean depth of the lake or reservoir, and was first used by Ryder (1965) to estimate the fishing yield of African lakes. Oglesby (1977) found that a better fit could be obtained for MEI expressed as the relation between conductivity and the average depth:

$$\text{MEI} = \frac{\text{conductivity } (\mu \text{S.cm}^{-1})}{\text{average depth (m)}}$$

13.3 Results

13.3.1 Relationships Between the Limnological Variables

The analysis shows that the TKN and total phosphorus acted positively to the development of chlorophyll-a concentrations, and the variables ammonia nitrogen and nitrate showed negative relationships with the variable. These results demonstrate the importance of nutrients in concentrations of chlorophyll-a in the reservoir. The model predicts 28% of the relationship of independent variables on chlorophyll-a ($R = 0.527$, $R^2 = 0.278$, $N = 278$, $F = 26.254$) (Table 13.1), according to the following model:

Analysis for testing the relationship between water transparency and other forms of nutrients which help to increase the concentration of chlorophyll-a was of the stepwise type, where the variables that show $p > 0.05$ are successively discarded from the model (Table 13. 2). The final multiple regression model explains 30% of the variability of chlorophyll-a

Table 13.2 Results of multiple regression analysis assessing the effect of water transparency, TKN, and ammonia nitrogen variables on concentrations of chlorophyll-a in the Itaipu Reservoir for the period from 1999 to 2004

	Coefficient	Std. error	T	*p*	VIF
Constant	0.651	0.156	4.160	<0.001	
Transparency	−0.505	0.111	−4.566	<0.001	1.020
Ammonia nitrogen	−0.241	0.106	−2.268	0.024	1.098
TKN	0.749	0.0814	9.200	<0.001	1.11

Table 13.3 Results of multiple regression analysis assessing the effect of water transparency, TKN, BOD, and COD on concentrations of chlorophyll-a in the Itaipu Reservoir, for the period from 1999 to 2004

	Coefficient	Std. error	T	*p*	VIF
Constant	0.698	0.0797	8.756	<0.001	
Water transparency	−0.484	0.108	−4.497	<0.001	1.026
TKN	0.626	0.0776	8.068	<0.001	1.074
COD	0.170	0.0835	2.040	0.042	1.188
BOD	0.462	0.138	3.347	<0.001	1.242

Table 13. 4 Results of multiple regression analysis assessing the effect of variables ammonia nitrogen, chlorophyll-a, turbidity, TKN, total suspended solids, BOD, and total phosphorous on the water transparency in the Itaipu Reservoir, for the period from 1999–2004

	Coefficient	Std. error	T	*p*	VIF
Constant	0.337	0.0728	4.627	<0.001	
Ammonia nitrogen	0.0820	0.0383	2.141	0.033	1.197
Chlorophyl-a	−0.0724	0.0213	−3.401	<0.001	1.491
Turbidity	−0.236	0.0250	−9.466	<0.001	1.380
TKN	0.0971	0.0332	2.921	0.004	1.549
Suspended solids	−0.210	0.0254	−8.273	<0.001	1.370
BOD	0.184	0.0497	3.691	<0.001	1.270
Total phosphorous	−0.145	0.0248	−5.852	<0.001	1.210

(R = 0.550, R^2 = 0.302, F = 39.586, N = 278, $p \leq 0.05$), being expressed by the following model. According to this analysis, the concentration of chlorophyll-a (dependent variable) can be explained by a linear combination of independent variables, indicating that all the variables tested contributed to the development of phytoplankton, while the only negative effect was the variable water transparency.

In order to establish which other variables contributed to the development of phytoplankton (through chlorophyll-a concentration), another multiple regression analysis was performed (Table 13.3). The results show that besides TKN, the independent variables BOD and COD were significantly correlated with chlorophyll (Table 13.7). The final accepted model explains 35% (R = 0.589, R^2 = 0.347, F = 36.270, N = 278, $p \leq 0.05$) ratio of chlorophyll-a over the other variables:

$$\log \text{chlorophyll} - a = 0.698 - (0.484 \times \log \text{seechi}) + (0.626 \times \log \text{TKN}) + (0.170 \times \log \text{COD}) + (0.462 \times \log \text{BOD})$$

To prove the effects of water transparency on the productivity of the reservoir, a multiple regression analysis was performed to identify independent variables that are significantly correlated with water transparency (Table 13.4). The result of this analysis demonstrates the importance of independent variables tested on water transparency. These responses explain 61% of the relationship significantly correlated with the tested independent variables (R = 0.783, R^2 = 0.613, F = 61,019, N = 278, $p \leq 0.05$), having chlorophyll, turbidity, and suspended solids influenced the model negatively, and ammonia nitrogen, TKN, and BOD positively. The model generated in this analysis was:

$$\begin{aligned}\ln \text{Secchi} = {} & 0.337 + (0.0820 \times \ln \text{ammonia nitrogen}) \\ & - (0.0724 \times \ln \text{chlorophyll-a}) - (0.236 \times \ln \text{turbidity}) \\ & + (0.0971 \times \ln \text{TKN}) - (0.210 \times \ln \text{suspended solids}) \\ & + (0.184 \times \ln \text{BOD}) - (0.145 \times \ln P \text{ total})\end{aligned}$$

13.3.2 Trophic State Index

Figure 13.3 shows the values of the weighted average (Secchi disk, chlorophyll-a, and total phosphorous) of Trophic State Index. The transition zone showed the highest average (49.44), with the highest value (69.67) in August 2001. The

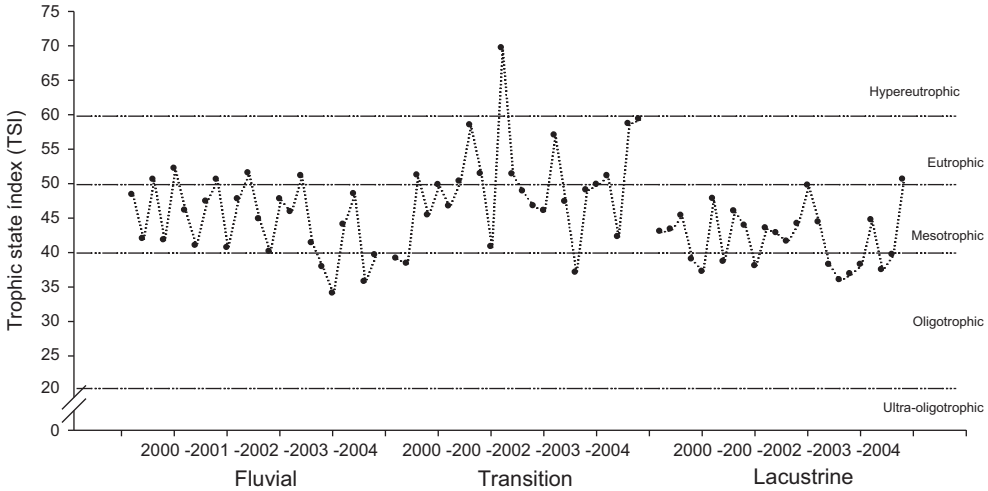

Fig. 13.3 TSI variation (average) in the Itaipu Reservoir for the period from 1999 to 2004

riverine zone presented an average of 52.19, with the lowest value (34.08) in November 2003. The lacustrine zone had the lowest average among the zones of the reservoir, with an average of 36.02.

The calculation of TSI average for the entire reservoir was 45.40, what can be classified as mesotrophic. This value, however, is near the threshold value of the oligotrophic waters classification (≥44).

13.3.3 Density and Relative Abundance of Phytoplankton

Figure 13.4 shows the relative abundance of phytoplankton in the Itaipu Reservoir. Cyanobacteria were abundant in the whole system, comprising 76% of the total. In the transition zone relative abundance was 90% whereas in the riverine zone it was 65%. The diatoms corresponded to the second most abundant group, with 14% of the total. In the riverine zone we obtained the greatest concentration (23%) and the smallest contribution was in the transition zone (7%). Chlorophyceae accounted for 5%, being more abundant in the riverine zone (9%) and less abundant in the transition zone (2%). The same pattern was found for the phytoflagellates with a frequency of 5% for the whole reservoir, with greatest abundance recorded in the area lacustrine zone (7%) and lowest in the transition zone (2%).

13.3.4 Density and Relative Abundance of Zooplankton

The relative abundance of the zooplankton groups can be seen in Fig. 13.5. Copepods were abundant in the entire reservoir, and in the lacustrine zone we obtained its highest value (58%). In the transition zone abundance was 54% and in the riverine zone 42%. The rotifers corresponded to the second most abundant group, with 32% for the entire reservoir. In the riverine zone we obtained the highest value (44%), in the transition zone 28%, and in the lacustrine zone we verified the lowest relative abundance (25%).

Cladocerans showed the lowest relative abundance throughout the whole reservoir, with 17%. The highest abundance was in the transition zone (18%), similar to the lacustrine zone (17%), with the smallest contribution occurring in the riverine zone (14%).

13.3.5 Fishes

Figure 13.6 shows the relative abundance of groups of fishes in the riverine, transition, and lacustrine zones of the Itaipu Reservoir. The omnivores were the most abundant group throughout the reservoir, with 47.2%, followed by piscivores (30.5%), zooplanktivores (8.5%), detritivores (6.2%), iliophagous (5.7%), benthivores (1.1%), insectivores (0.5%), and herbivores (0.3%). In the lacustrine zone omnivores were more abundant (71.8%), followed by detritivores (14.9%), and piscivores (8.7%). The other groups showed low abundance, and no presence of benthivores was recorded in this region. The transition zone also showed a higher relative abundance of omnivores (38.3%), followed by piscivores (37.2%). The iliophagous had 11.2% of relative abundance, followed by zooplanktivores (10.6%), detritivores (1.4%), benthivores (0.7%), herbivores (0.6%), and insectivores (0.1%). In the lacustrine zone the highest relative abundance pertained to piscivores (45.6%), followed by omnivores (31.5%), zooplanktivores (14.2%), iliophagous (3.1%), benthivores (2.7%), detritivores (2.2%) and, finally, herbivores and insectivores (0.3%).

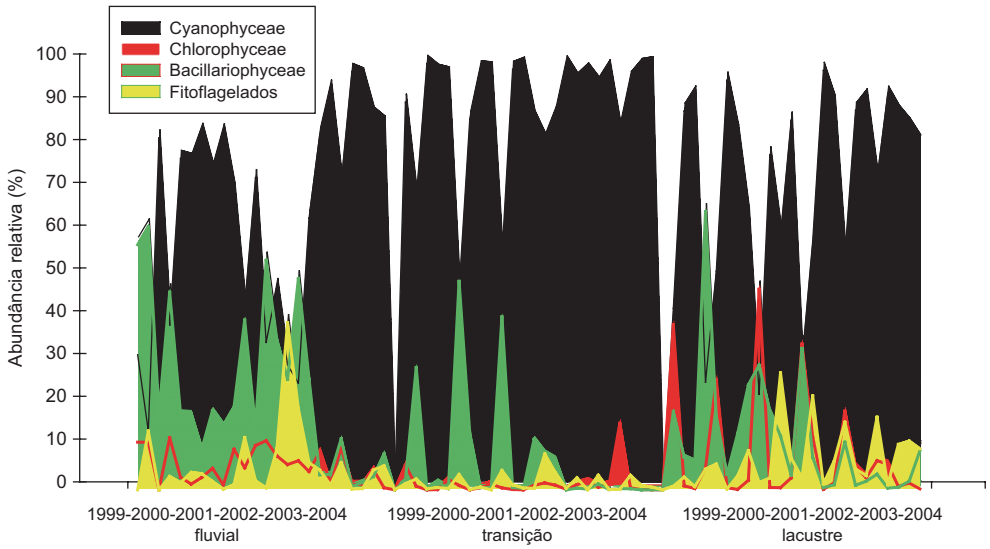

Fig. 13.4 Variation of the relative abundance of phytoplankton according to the zones of the Itaipu Reservoir for the period from 1999 to 2004

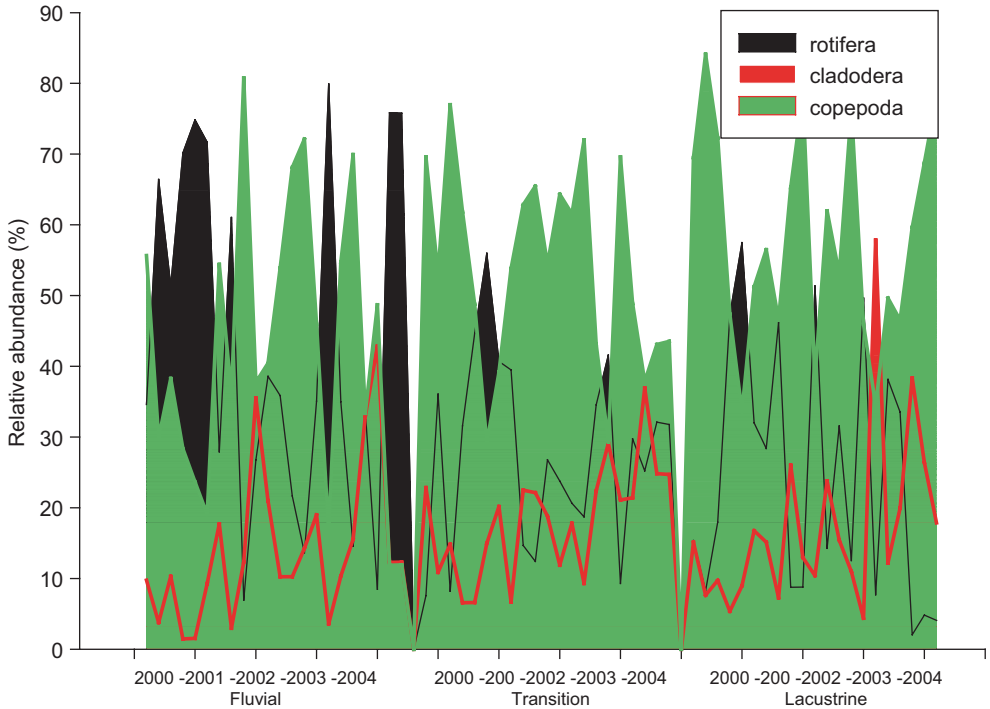

Fig. 13.5 Variation of the relative abundance of zooplankton according to zones of the Itaipu Reservoir for the period from 1999 to 2004

13.3.6 Analysis of Trophic Interactions in the Itaipu Reservoir: Direct Effects

Table 13.5 shows the negative impact of suspended solids concentration and turbidity on the Secchi disk value. In other words, the higher the concentrations of these variables, the lower are the values of the Secchi disc reading, and consequently, of water transparency.

To test the trophic cascade hypothesis in the reservoirwe performed linear regression analyses, checking the trophic levels one by one, thus determining the interactions between them (Table 13.5).

The omnivorous fishes showed to be negatively dependent on the piscivores, that is, the higher the piscivore biomass is, the lower the omnivore biomass will be. The benthivores were dependent on piscivores (positively) and negatively dependent on omnivores. The detritivores were dependent on omnivores (positive relationship) and negatively dependent on piscivores. The zooplanktivorous fishes proved to be dependent on piscivores (positive relationship) and negatively dependent on omnivores.

Table 13.5 shows the relationships between macrozooplankton groups and fish trophic guilds. Both copepods and cladocerans had positive relationships of dependence with iliophagous fish biomasses.

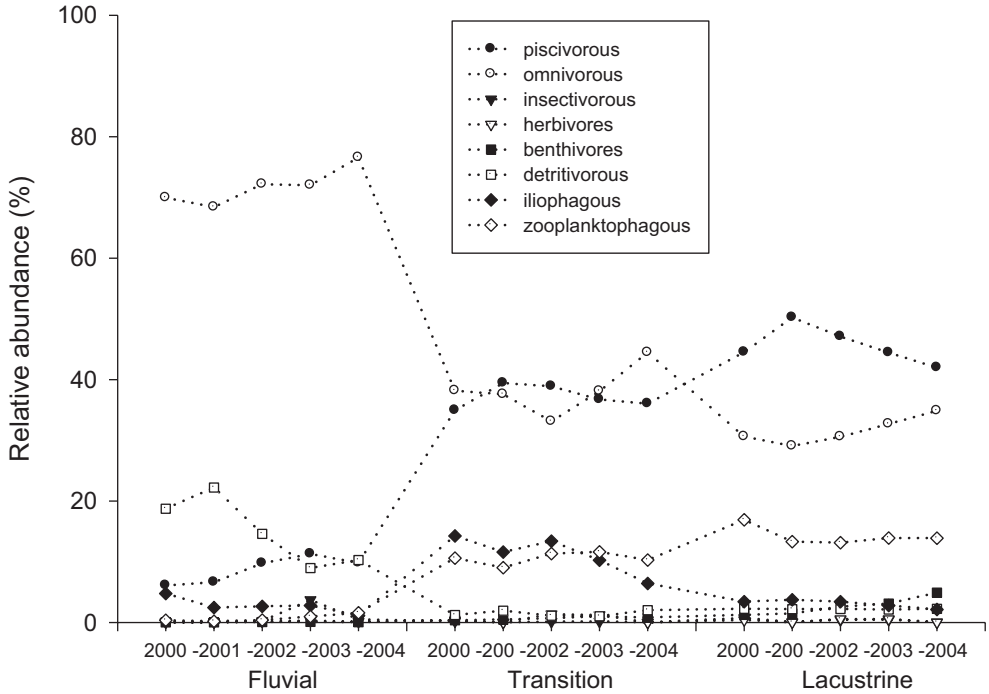

Fig. 13.6 Variation of the relative abundance of fish trophic guilds according to zones of the Itaipu Reservoir for the period from 2000 to 2004

Table 13.5 Models of linear regressions performed and their respective values of R^2, R, F, and *p*

Models of linear regressions	Effect	R^2	R	F	*p*
log secchi = 0.287 – (0.368 * log suspended solids)	–	0.412	0.642	200.607	<0.001
log secchi = 0.390 – (0.345 * log turbidity)	–	0.372	0.610	169.063	<0.001
log omnivores = 7.241 – (0.452 * log piscivores)	–	0.624	0.790	21.544	0.000
log benthivores = −8.618 + (2.410 * log piscivores)	+	0.875	0.935	90.620	0.000
log detritivores = 9.516 – (1.154 * log piscivores)	–	0.565	0.752	16.896	<0.001
log zooplanktivores = −5.077 + (1.899 * log piscivores)	+	0.904	0.951	122.815	0.000
log benthivores = 21.538 – (3.663 * log omnivores)	–	0.662	0.813	25.419	<0.001
log detritivores = −9.124 + (2.583 * log omnivores)	+	0.928	0.963	166.702	<0.001
log zooplanktivores = 19.857 – (3.117 * log omnivores)	–	0.797	0.893	51.156	<0.001
log copepoda = −2.721 + (1.739 * log iliophagous)	+	0.583	0.763	18.169	<0.001
log cladocera = −2.493 + (1.569 * log iliophagous)	+	0.610	0.781	20.344	<0.001
log chlorophyll-a = −0.274 + (0.303 * log cladocera)	+	0.301	0.549	6.901	0.018
log chlorophyll-a = −0.0155 + (0.209 * log copepoda)	+	0.186	0.431	3.657	0.074
log chlorophyll-a = 0.563 + (29.689 * log P total)	+	0.162	0.402	3.084	0.098
log chlorophyll-a = 6.145 – (1.029 * log omnivores)	–	0.319	0.565	6.082	0.028
log chlorophyll-a = 1.699 – (0.294 * log insectivores)	–	0.364	0.603	7.436	0.017
log chlorophyll-a = 2.573 – (0.415 * log detritivores)	+	0.372	0.610	7.696	0.016
log cyanobacteria = −2.354 + (0.808 * log iliophagous)	+	0.537	0.733	15.067	0.002
log P.total = 0.0234 – (0.00442 * log insectivores)	–	0.453	0.673	10.770	0.006
log P.total = 0.0169 – (0.00243 * log herbivores)	–	0.443	0.665	10.323	0.007
log cyanobacteria = 17.850 – (2.823 * log omnivores)	–	0.658	0.811	24.980	<0.001
log cyanobacteria = 4.969 – (0.543 * log insectivores)	–	0.341	0.584	6.725	0.022
log cyanobacteria = 7.750 – (1.060 * log detritivores)	–	0.667	0.817	26.042	<0.001
log cyanobacteria = 1.167 + (0.586 * log zooplanktivores)	+	0.346	0.588	6.864	0.021
log cyanobacteria = −0.349 + (0.359 * log cyanobacteria)	+	0.520	0.721	17.345	<0.001

Table 13.6 Summary of results of multiple regression analysis assessing the effect of chlorophyll, water transparency, turbidity, total suspended solids variables, and TKN on the densities of cyanobacteria in the Itaipu Reservoir

	Coefficient	Std. error	T	*p*	VIF
Constant	0.700	0.408	1.718	0.087	
Chlorophyll-a	1.536	0.160	9.611	<0.001	1.057
Transparency	1.518	0.613	2.475	0.014	1.567
Turbidity	0.417	0.190	2.197	0.029	1.450
Suspended solids	−0.501	0.239	−2.098	0.037	1.554
TKN	3.420	1.047	3.266	0.001	1.091

Table 13.7 Summary of results of multiple regression analysis assessing the effect of P total and omnivores variables on concentrations of cyanobacteria in the Itaipu Reservoir

	Coefficient	Std. error	T	*p*	VIF
Constant	17.622	2.499	7.053	<0.001	
log total phosphorous	45.331	20.048	2.261	0.043	1.003
log omnivores	−2.883	0.493	−5.849	<0.001	1.003

The abundance of cladocerans and copepods positively interfere in the concentration of chlorophyll-a, that is, the more abundant are these groups are, the greater the concentration of chlorophyll-a will be. Observing the dependence of the chlorophyll-a in relation to the previous level, it is possible to see that the total phosphorus positively affects the concentration of chlorophyll-a (Table 13.5).

13.3.7 Analysis of Trophic Interactions in the Itaipu Reservoir: Indirect Effects

Table 13.5 presents the indirect relationships between chlorophyll-a and fish trophic guilds in the reservoir. The groups of fish that had an influence on chlorophyll-a concentrations were: omnivores and insectivores (negative relationship), and detritivores and iliophagous (positive relationship).

Table 13.5 presents the results of indirect interactions between the concentration of total phosphorus and groups of fishes. Insectivores and herbivores were the groups of fishes that showed negative interference on the concentrations of total phosphorus.

Table 13.5 shows the results of indirect interactions between the cyanobacteria biomass and groups of fishes. Omnivores, detritivores, and insectivores showed negative interference on the abundance of cyanobacteria, while zooplanktivores had a positive relationship.

Table 13.5 shows the positive dependence between chlorophyll-a and cyanobacteria, indicating that the increased concentration of cyanobacteria favors increased chlorophyll-a concentration.

13.3.8 Analysis of the Relationship Between Cyanobacteria and Total Phosphorus and Fishes in the Itaipu Reservoir

The analysis of Table 13.6 shows that the cyanobacteria were correlated with limnological variables, to reveal which of them had relationships with a dependent variable. This analysis indicated that the density of cyanobacteria had significant positive dependence on chlorophyll-a, water transparency, turbidity, suspended solids, and TKN. Only the concentration of suspended solids showed negative interference on them. The multiple regression model explained 33 % of the variability of cyanobacteria ($R=0.571$, $R^2=0.326$, $F=27{,}334$, $N=288$, $p=0.05$), as expressed by:

$$\ln \text{cyanobacteria} = 0.700 + (1.536 \times \ln \text{chlorophyll}) + (1.518 \times \ln \text{sec chi}) + (0.417 \times \ln \text{turbidity}) - (0.501 \times \ln \text{suspended solids}) + (3.420 \times \ln \text{TKN})$$

The biomass of cyanobacteria was correlated with P total and omnivores biomass. Phosphorus showed a positive relationship, favoring the development of cyanobacteria and a negative relationship regarding omnivores (cyanobacteria control). The results were $R=0.872$, $R^2=0.760$, $P=<0{,}001$ $F=18.998$, $N=15$, $p=0.05$ (Table 13.7). The model generated from this analysis was:

$$\ln \text{cyanobacteria} = 17.622 + (45.331 \times \ln P \text{ total}) - (2.883 \times \ln \text{omnivores})$$

Table 13.8 Summary of results of multiple regression analysis assessing the effect of total phosphorous and detritivores variables on concentrations of cyanobacteria in the Itaipu Reservoir

	Coefficient	Std. error	T	*P*	VIF
Constant	7.320	0.713	10.268	<0.001	
Total phosphorous	48.976	18.973	2.581	0.024	1.007
Detritivores	−1.097	0.174	−6.309	<0.001	1.007

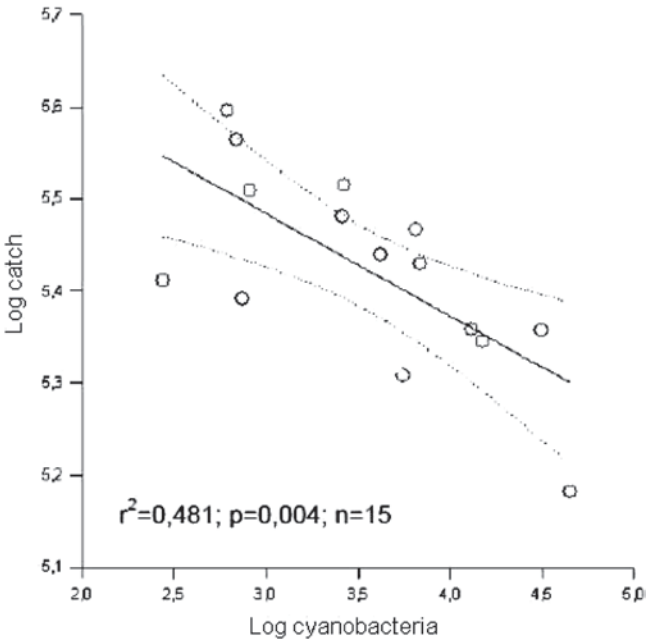

Fig. 13.7 Regression analysis between cyanobacteria log and capture log in the Itaipu Reservoir for the period from 2000 to 2004

Cyanobacteria were also correlated to the concentration of total phosphorus and to detritivorous fishes. Cyanobacteria also developed when there was an increase in P total and showed a negative relationship with detritivores (Table 13.8). These results indicate that the limiting nutrient for the development of these algae is P total and that the fishes also play a critically important role in this environment. These results can be observed in linear regression analyses that were performed in studies of trophic-level relationships (*a posteriori*).

The multiple regression model explained 78% of the variability of chlorophyll-a ($R=0.887$, $R^2=0.786$, $p=0.001$, $F=22.025$, $N=15$) and this can be expressed by the model:

$$\ln \text{cyanobacteria} = 7.320 + (48.976 \times \ln P \text{ total}) - (1.097 \times \ln \text{detritívores})$$

13.3.9 Inference of Fish Yield

Figure 13.7 depicts the regression between the capture and the logarithm values of cyanobacteria densities. This relationship proved to be negative, indicating depletion of capture when there was an increase in cyanobacteria. The values of the correlation coefficient explain 47% of the model at 0.05 significance.

The results of the inference of fish production by means of empirical models for the Itaipu Reservoir are shown in Fig. 13.8. According to this inference, the reservoir had an average fishing yield of 8.1 kg/ha/year. The transition and riverine zones had the highest mean productivity (8.2 kg/ha/year), while the lacustrine zone obtained an average yield of 8.1 kg/ha/year.

13.4 Discussion

13.4.1 Limnology of the Itaipu Reservoir

Limnological variables are of crucial importance to characterize the zones of a reservoir. According to its longitudinal variation, to the sedimentation of allochthonous and autochthonous material in the environment, a reservoir has essentially three main zones: the riverine region, the transition region, and the lacustrine region (Tundisi 1990). These regions have a horizontal distribution, with their own dynamics, being influenced by inflowing water from rivers and by the outflow of water through spillways and turbines.

The Itaipu Reservoir shows strong relations between the riverine, transitional and lacustrine zones. According to Thornton (1990) these relationships suggest that the seasonal variability can be explained by the hydrodynamic process, especially because of the discharges that the Rio Paraná suffers, causing an irregular dynamics of the limnological variables.

The analyses of this study indicated that the Itaipu Reservoir showed horizontal spatial heterogeneity for some limnological and biological variables. When one examines the topographical map of the valley of the Itaipu Lake (Stivari et al. 2005), it is evident that the topography of the transition zone favors increased water inflow (Tucci 2002), explaining a major input of allochthonous material to the reservoir.

Ferrareze et al. (2005) evaluated the transportation of nutrients and suspended material in different parts of the Paranapanema River and its tributaries. The results explain the importance of the hydrological cycle, in particular precipitation, and of the lateral and longitudinal dimensions.

The use and occupation of land is an extremely important factor in reservoir studies. Activities such as monoculture and large areas of pasture may increase concentrations

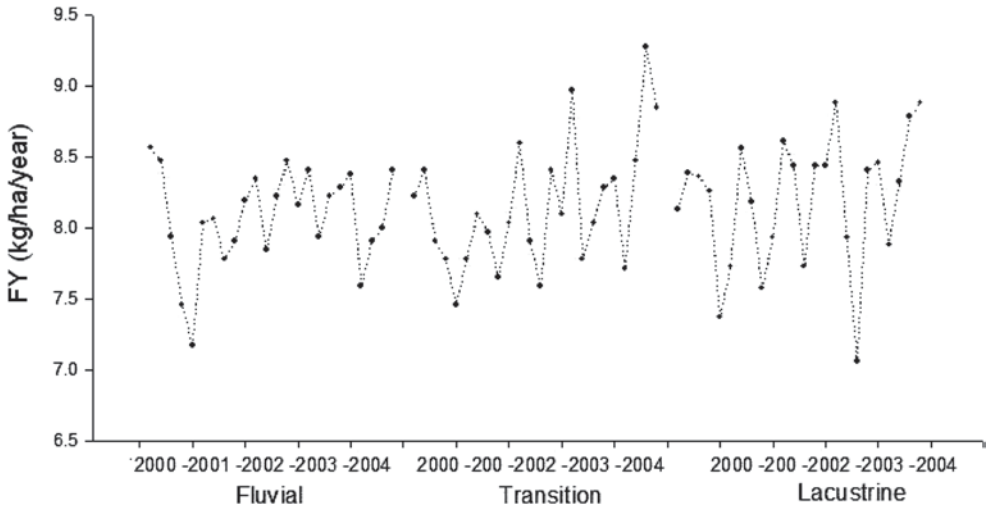

Fig. 13.8 Estimates of fishing yield (FY) in kg/ha/year according to the zones of the Itaipu Reservoir, for the period from 1999 to 2004

of nutrients in the aquatic ecosystem. On the banks of the reservoir, on the Brazilian side, there are large areas that contribute to the acceleration of eutrophication of the reservoir (diffuse pollution), while on the Paraguayan side there are still large areas of forests along the reservoir.

A study in the São Simão Reservoir (MG) showed that the highest concentrations of nutrients and solids flowing into the reservoir were found in rivers where there was agriculture and livestock (Pinto Coelho et al. 2005). The same effect can be observed in cascade reservoirs of the Paranapanema River (Nogueira et al. 2005).

Temperature is one of the most important variables (a) in the distribution and physiology of aquatic organisms, what may cause altercations in the dynamics of nutrients in the water column (Esteves 1988) and (b) in studies of the food web and biomanipulation in lakes and reservoirs, influencing the metabolic rates of fish (Jezierska 1979). The ammonia excretion rates increase with the increase of this variable (Iwakuma et al. 1990) and phosphorus cycling by fish is accelerated (Andersson et al. 1988; Persson 1997). In the Itaipu Reservoir water temperature showed a distinct pattern of seasonal variation, with the highest temperatures recorded between November and March and the lowest from May to August. The highest temperature was found in the lacustrine zone (30.4°C). These data are consistent with those described by Agostinho et al. (1997b) and Andrade et al. (1988), and in reservoirs located in the Serra do Mar, state of Paraná (Pagioro et al. 2005a).

Water transparency has a strong influence on the trophic aquatic environments, and penetration of light determines the development of phytoplanktonic organisms and therefore environmental enrichment (Esteves 1988; Wetzel 1990; Henry 1990). In addition to the input of allochthonous material, which is transported and sedimented in water, contributing to the reduction of water transparency, high fish biomasses can also reduce water transparency (Shapiro et al. 1975; Mcqueen et al. 1990; Sondergaard et al. 1997) because of increased nutrients owing to the excretions of fishes (Drenner et al. 1996; Starling 1998).

In the Itaipu Reservoir the lowest water transparencies were recorded in the riverine zone owing to the transportation of particles and sedimentation rates, which are directly associated with the inflow of water courses. The data analysis of suspended solids indicates that, as this variable diminishes, water transparency increases, as noted by Andrade et al. (1988), Agostinho et al. (1997).

The values of water transparency were related with some limnological variables and the results indicate that the chlorophyll-a, turbidity, suspended solids, and total phosphorus variables influenced negatively water transparency. This can be explained by the fact that when the independent variables increase in value, the dependent variable increases, interfering directly in the amount of light in the system. The variables ammonia nitrogen and TKN showed a positive effect, contributing to the increase in water transparency. This occurred because the forms of nutrients are related with the increase of primary productivity, indicating casual relations, so that these variables have their effects limited by the availability of light into the water environment.

The concentration of suspended solids in the water, besides the water cycle and turbidity, is also one of the most important limiting factors to primary production in environments that present high values of this variable, influencing the photosynthetic behavior and causing changes in the ecology of the ecosystem (Calijuri and Tundisi 1990). It is important to note that climatic factors such as rainfall play an important role especially with regard to the water transparency variable. The results of the analyses comparing rainfall and water transparency demonstrate the negative effect, what means that this variable is of great importance to measure the productivity of aquatic environments. Souza Filho and Stevaux (1997) emphasize that the discharge of solids in the Paraná River was at around 30 million tons per year, of

which only 10% refer to bed material load. The suspended load varies according to the flood peaks (precipitation).

The turbidity of water the measurement that expresses the loss of light penetration into the aquatic environment, as it is a result of all organic and inorganic material that is in suspension in water in the form of particles (Wetzel 2001). In the Itaipu Reservoir this variable showed very similar values among the riverine, transition and lacustrine zones, although it presented declining average values in the upstream-downstream direction, confirming the results of Andrade et al. (1988). The highest values of turbidity can be explained by occasional periods of rain just before and during the collection of data, as observed by Zanata (1999) in Salto Grande reservoir (Americana, SP) and by Pinto Coelho *et al.* (2005) in São Simão Reservoir (MG). This variable is very important because many species of predator fishes have a visual active persecution feeding tactics (Ribeiro filho 1999), promoting the resuspension of organic and inorganic materials as they move around to catch food (Pedro 1995). This variable is directly related to the decrease in water flow, resulting in a lower input of suspended materials in the water.

According to Esteves (1998), the pH represents the ionic balance in the aquatic environment, interfering directly with the conditions of neutrality of water and environmental buffering capacity (alkalinity). The increase of this variable may be related to changes in the values of alkalinity in aquatic ecosystems, explaining the inverse relationships of the alkalinity values found with regard to pH. The Itaipu Reservoir, in general, presented an alkaline pH with slight tendency to neutrality. These results are in consonance with those by Agostinho et al. (1997a). The fact that the transition zone presents higher pH values may be related to higher photosynthetic activity (cyanobacteria) in this region (Vollenweider 1974). Shapiro and Wright (1984), in an experimental study, found that concentrations of pH and CO_2 are variables that help to determine the cyanobacteria populations.

Electrical conductivity is the resistivity ability to transmit electricity in the water body, reflecting indirectly the level of dissolved solids in water. In some studies the increase in conductivity was accompanied by the increase of cyanobacteria (Ramirez 1996). In the Itaipu Reservoir, although quite discrete, the highest conductivity was recorded in the transition zone. The exclusive presence of tilapia (*Oreochromis niloticus* and *Tilapia rendalli*) when compared to treatments without the presence of fishes in studies by Starling and Rocha (1990) and Figueredo (2000), showed an increase in the values of electrical conductivity as a result. The ion concentrations in the lacustrine area can be explained by the higher biomass of piscivore species, justified by the control of omnivore biomass (Ribeiro Filho 2002).

The dissolved oxygen in the aquatic ecosystem is a limiting factor for both nutrient cycling and for primary productivity (Agostinho et al. 1997a). In this study, we observed a pattern in their distribution with regard to seasonality during the months the data were collected, confirming the results reported by Agostinho et al. (1999), in which the lowest dissolved oxygen concentrations were found in summer (January to March) and the highest during the rainy season (June to August). For this work, the highest amount of dissolved oxygen in the transition zone may be associated with the great development of algae, especially cyanobacteria. The month of March, for all years, presented the lowest concentration of this gas, as it is strongly affected by water temperature (in warmer months there is loss of oxygen into the atmosphere and increased metabolism of the environment).

In a study by Minillo (2005) in reservoirs in the middle and lower Tietê River (SP) high concentrations of dissolved oxygen were found in the water surface. The author stresses that these findings may be related to the rainy months and other studies also emphasize the effect of rainfall in the distribution pattern of dissolved oxygen (Townsend 1999).

The BOD variable represents the amount of oxygen required to oxidize organic matter by microbial decomposition. The increase in the values of this variable represents an increase of organic or punctual pollution (CETESB 2006). The transition zone showed the highest mean values owing to swine breeding activity in that area of the watershed (Benassi, personal communication, 2006).

The COD variable represents the amount of oxygen required to oxidize organic matter by means of chemical agents. The increases in the DQO values in water bodies are indicative of industrial pollution (CETESB 2006). As with the BOD, COD showed a higher average concentration in the transition zone (7.5 mg/L), which can also be associated with the input of materials into the reservoir.

The nitrogen and phosphorus are the main nutrients for aquatic environment primary producers (Esteves 1988) and the mean increase of nutrients means changes in the abundance of fishes, in what regards composition and biomass in temperate lakes (McQueen 1998). The fish biomass and their density per unit area of the lake increase with increasing concentration of total phosphorus (Hanson and Lagget 1982; Quiros 1990), so that the concentration of predatory fishes is reduced (Jeppesen et al. 1990; Persson et al. 1988).

Among the nitrogen forms mostly consumed by the communities of aquatic ecosystems are ammonia nitrogen, nitrate, and nitrite. Nitrite is the intermediate state between ammonia and nitrate, during the nitrification process, and is not very much available in the environment and used by primary producers. Nitrite is a very complex variable, because it is converted into ammonia or nitrate and unlikely to accumulate in the system, what explains the lack of relationship with chlorophyll-a. Their low concentrations may also indicate a high oxygen environment (Esteves 1988).

The nitrate concentrations in the reservoir had a horizontal longitudinal distribution. The results were similar to those

found previously in the Itaipu Reservoir (Agostinho et al. 1999), but in lower concentrations. Ammonia nitrogen is the least found nitrogen form and one of the most frequently used by primary producers. This is because the ammonium ion can be used as a nitrogen source during protein synthesis by primary producers. This may happen as ammonia is one of the main forms of nitrogen excreted by fishes (Wetzel 1993). In the Itaipu Reservoir the average concentration of this variable was 0.03 mg/L, confirming the results of Agostinho et al. (1997b), with average values of 0.033 mg/L.

The total TKN is the sum of forms of organic and ammonia nitrogen, which are extremely important for biological activity. In the Itaipu Reservoir this form of nutrient was the one which presented the best relationship with the chlorophyll-a concentrations, and positive relationship with water transparency, as evidenced by multiple regression analysis. The concentrations of total Kjeldahl nitrogen in the reservoir had horizontal distribution similar to that found by Agostinho et al. (1999) and Andrade et al. (1988), with the transition zone having higher concentrations of this nutrient. This was the variable that best correlated with the chlorophyll-a variable, corroborating the results found by BINI (2003), thus demonstrating the assimilation of this source of nitrogen by phytoplankton (Reynolds 1984; Esteves 1988). The relationship between the nitrogen forms of chlorophyll was also observed by Kurmayer and Wanzenbock (1996) and Karjalainen et al. (1998), who found a direct relationship between the reductions in nitrate and ammonia concentrations and increase in concentrations of chlorophyll-a in experiments in ponds with known fish biomasses.

Phosphorus is found in the aquatic environment in the same way that nitrogen is (organic and inorganic/in particles and dissolved) and together they are the most important nutrients for primary production in aquatic ecosystems. The lowest average concentration in the lacustrine zone of Itaipu Reservoir can be explained by sedimentation rates throughout the watercourse. It is important to stress that the P total in this zone may have more effect on productivity (chlorophyll-a) owing to the luminosity factor (Pagioro and Thomaz 2002). This explains why the phosphorus had no significant relationship when related to chlorophyll-a and water transparency in the multiple regression analysis of the Itaipu Reservoir.

Comparing the total phosphorus concentrations with the results Agostinho et al. (1999) and Andrade et al. (1988), it is possible to observe that the reservoir presented a seasonal longitudinal distribution pattern that is similar in both studies. The concentrations of this nutrient were similar in both studied zones (Agostinho et al. 1999) and this showed that the constant reduced concentrations of total phosphorus is an important implication for the absence of eutrophication in the Itaipu Reservoir. Tundisi et al. (1993) point out that inhibition of the eutrophication process can be associated with the retention of this nutrient in cascade systems reservoirs located upstream of the Itaipu Reservoir, and studies conducted by Nogueira et al. (2005) show a decrease of phosphorus in cascade systems reservoirs. Furthermore, Agostinho et al. (1999) point out that large sources that carry phosphorus into the reservoir are limited by the tributaries and the floodplain.

The impact of fish that feed on sediment detritus, making available large concentrations of phosphorus for phytoplankton has been studied by several authors (Lamarra 1975; Drenner et al. 1996; Persson 1997; Starling 1998). In Paranoá Lake this impact was observed in the stock of tilapia owing to their omnivorous feeding habits, more than 50 % of their stomach contents consisted of sediment in the study by Grando (1989), what through excretion is released into the water column, increasing the concentration of phosphorus (Pereira and Ribeiro Filho 2004).

The primary productivity, which can be expressed indirectly by the concentration of chlorophyll, is controlled by the action of light and nutrient factors (Henry and Simon 1990), considered fundamental to the development of phytoplankton productivity in freshwater ecosystems.

The horizontal distribution of chlorophyll-a concentrations in the Itaipu Reservoir showed significant relationships with almost all forms of nutrients. The multiple regression analysis indicates that the nitrate and ammonia nitrogen negatively affect primary productivity, while the total Kjeldahl nitrogen and total phosphorus positively affected the primary productivity. These results corroborate those by Pagioro et al. (2005b) in six reservoirs in the state of Paraná, where they found similar effects of nutrients on chlorophyll-a and verified the same pattern of distribution.

The phytoplankton community of a reservoir is maintained by continuous input of nutrients (inflows) and by the nutrients recycled by zooplankton and fishes. A way commonly used to quantify the amount of algae in a specific reservoir is by determining the concentrations of chlorophyll-a (Straskaba and Tundisi 2000).

The pattern of longitudinal distribution of chlorophyll-a in the reservoir was constant for the riverine and lacustrine zones, where the average concentrations found were similar. On the other hand, the transition zone, whose highest concentrations of chlorophyll were associated with higher nutrient concentrations, showed a distribution related to the seasonality of rainfall. Studies by Andrade et al. (1988) corroborate the results of the present study. The highest concentrations of chlorophyll-a in the Itaipu Reservoir, in the transition zone, are explained by higher concentrations of total Kjeldahl nitrogen, total phosphorus and nitrate, and, apparently, these correspond to the forms of nutrients that were influential in increasing concentrations of chlorophyll-a. Pagioro et al. (2005b) commented that the prevalence of high concentrations of chlorophyll-a in the intermediate zones (transition) are owing to the ideal relationship between light

and phosphorus, most found in these regions, increasing primary productivity. The authors emphasize that this pattern in the distribution of chlorophyll-a is not always found and this is because other factors (such as residence time, reservoir size, morphometry) influence the metabolism of primary productivity.

It is important to stress that the impact of diffuse pollution (agricultural) and punctual pollution may be increasing nutrient levels in the Itaipu Reservoir, as it can be seen in satellite images of the region where the Itaipu Reservoir is located (Stivari et al. 2005). Another aspect to be analyzed with regard to the transition zone is that, besides a steeper topography, a large swine farming activity is practiced in the São Francisco Verdadeiro e Falso River micro basins, producing pollution owing to an increase in nutrients caused by lack of waste treatment of these farms (Benassi, S.F., personal communication). Most of these properties are located near the banks of tributaries of the reservoir, explaining the increase of nutrient concentrations, and consequent higher occurrence of cyanobacteria in this region.

13.4.2 Trophic State Index (TSI)

The Trophic State Index is intended to classify water bodies according to nutrient enrichment and is obtained through statistical analysis of linear regression models (Toledo Jr et al. 1983). Water transparency many times does not show values that represent the trophic status of the environment, especially for the oligotrophic limit value. For this reason, we started to use the weighted average of the indices calculated by assigning a lower weight ratio to water transparency (Secchi disk reading), without having to remove it from the calculation of the TSI average.

The results obtained show that the transition zone has a higher trophic status than the other zones, what can be related to the higher nutrient input (diffuse pollution), as discussed above, or by the ratio of optimal light with the nutrient concentrations. The mean values of TSI indicate a slight improvement of the trophic state of water, according to spatial and temporal patterns. The values found for lacustrine zones indicate that these regions are oligotrophic. On the other hand, the riverine and transition zones showed higher values, reaching concentrations that indicate a mesotrophic level with some eutrophic values in the transition zone. Nevertheless, the average value for the entire reservoir, disconsidering the zone divisions, indicated that its waters can be classified as mesotrophic, corroborating studies by Andrade et al. (1988). These changes in trophic status among different regions were also found by Zanata (1999) and Minillo (2005), in which precipitation and diffuse pollution were the factors that best explained the changes of the trophic status.

Another important factor to consider is the cascade system upstream of the Itaipu Reservoir, present in the Tietê, Grande, and Paranapanema rivers, which supplies waters to the Paraná River, forming the reservoir. This factor may have a great influence, as the concentrations of nutrients and particulate matter undergo a lowering effect through the successive reservoirs in cascade systems (Nogueira et al. 2005; Andrade et al. 1988).

13.4.3 Analysis of Longitudinal Distribution of Biological Communities

The responses of the communities in reservoirs under manipulated conditions or not, are incomplete, as they are altered or destroyed before complete interactions. The instability of the formation of a new environment makes communities unstable owing to anthropogenic activities and damming (Agostinho and Gomes 2005). The process of spatial and temporal succession of communities in reservoirs depends on the speed of filling, withdrawal of vegetation or not, on the establishment of an extensive coastal zone which increases the substrate and the processes of colonization of the basin (Tundisi 1986a).

According to Tundisi (1990) the seasonal cycle of phytoplankton in reservoirs is due in large part to hydrodynamic changes. The pulses produce sudden changes in the system, with rapid discharges in the surface, producing impacts owing to the input of material in suspension, nutrient availability and solar radiation (which causes changes in the specific composition of the phytoplankton), as well as the frequency of turbulence caused by the action of winds (which affects the spatial distribution, horizontal and vertical of phytoplankton in reservoirs). The authors emphasize that the pattern of horizontal distribution determines the distribution characteristics of phytoplankton, resulting, in many cases, in algal blooms owing to the accumulation produced by the horizontal surface currents.

The relationship between the composition and distribution of phytoplankton and the physicochemical regimes are complex and the interaction can be understood only with long-term studies (Tundisi 1990). The variation in density, according to the main groups, shows a distribution pattern among the zones of the reservoir, in which we observed the dominance of cyanobacteria (76%) and that the remaining groups of algae were less abundant. These results corroborate those by Pinto Coelho et al. (2005), who obtained cyanobacteria abundances of values of 11,000 ind./mL, and Andrade et al. (1988), in the Itaipu Reservoir, with the highest densities of cyanobacteria *Mycrocystis kutzing*. Only in the transition zone cyanobacteria blooms were recorded, a fact that can be explained by higher nutrient availability in the rainy season and by the pH values (Shapiro and Wright

1984). One aspect that should be considered is the type of data collection, with water samples taken only from the surface, the area of greatest development of cyanobacteria (Tundisi 1990).

The low densities of phytoplankton groups studied can be justified by the low average concentrations of nutrients. According to Reynolds (1987), all phytoplankton species are likely to keep growing as long as nutrients are available, and faster growth species are selected in environments with favorable nutritional conditions.

The results of multiple regression analyses indicate that the independent variables water transparency, turbidity, and TKN showed a positive effect on the development of cyanobacteria in the Itaipu Reservoir, and the variable suspended solids influenced negatively in their development. The generated model can estimate the biomass of cyanobacteria from the independent variables mentioned above.

When cyanobacteria were related to total phosphorus and fishes, the results indicated that the limiting nutrient for the development of these algae is total phosphorus, and the fishes also play an extremely important role in this environment.

The proportion between the different groups that make up the zooplankton community(rotifers, copepods and cladocerans) is considered a way to use this community as an indicator of the trophic conditions of the environment, and the dominance of rotifers is often associated with increased eutrophication (Matsmura-Tundisi et al. 1990).

In the Itaipu Reservoir the most dominant group was Copepoda, with the highest densities in the whole system (57.97%). Studies in reservoirs of Paraná indicate the same dominance of copepods (Velho et al. 2005) and in the Tucuruí Reservoir, Espíndola et al. (2000) observed the same pattern. The highest density of Copepoda as well as of Cladocera, may be associated with a higher trophic level in the zones where the concentration of chlorophyll and cyanobacteria were higher. According Marzolf (1990), higher densities of zooplankton in the transition zone are observed when resource availability and hydrodynamics are interacting to determine abundance patterns.

The greatest abundance of zooplankton was recorded in the transition zone of the Itaipu Reservoir. Studies by Lansac-Tôha et al. (1999) in reservoirs of the state of Paraná showed results that corroborate the results of this work. The highest abundance in the transition zone is explained by higher concentrations of chlorophyll-a, owing to increased human activity observed in the basins of the San Francisco Verdadeiro e Falso Rivers, located in the transition zone. The distribution of small cladocerans may be related to the abundance of cyanobacteria, especially in eutrophic environments (Lansac-Tôha et al. 2005). The biochemical properties of cyanobacteria (and some species may be toxic) and the shape and size of colonies prevent an overexploitation of this resource by zooplankton, keeping the abundances of colonies stable (De Bernadi and Giussani 1999).

The second most abundant group was the rotifers. Although eutrophic and hyper eutrophic environments favor the dominance of rotifers, in most aquatic environments of Brazil, rotifers are often dominant, regardless of trophic status, both in density and in number of species (Rocha et al. 1995). The nondominance of rotifers in the Itaipu Reservoir (32%) is consistent with the results for oligotrophic and mesotrophic lakes in the USA (Blancher 1984), in which rotifers represent 20–37%.

Regarding the distribution of the longitudinal axis of the reservoir, the highest density of rotifers was found in the riverine zone and in the remaining zones there was a dominance of copepods. Studies in the reservoir of the Corumbá River (Lansac-Tôha 1999) show that the community structure was altered after the construction of the dam, when the densities of cladocerans and copepods showed greater development. Other authors relate the trophic status in the community structure of zooplankton (Matsmura-Tundisi et al. 1990; Lansac-Tôha et al. 2005).

The study of the determination of the time-space variation of fish communities and the way in which these stocks are removed from the environment are used to rationalize fishery management (Okada 2001). According to Hodgson et al. (1996) fish populations have effects of fundamental importance in trophic cascades, with direct influence on biomass and productivity of other trophic levels.

The results of the variation of the trophic structure of the fishes show that the group of omnivores was most abundant in the reservoir, followed by piscivores. These two groups accounted for 77.7% of the total biomass. The riverine zone showed higher occurrence of omnivores and detritivores. In the transition and lacustrine zones omnivores and piscivores were more abundant. Borghetti et al. (1988) also found eight trophic groups in the Itaipu Reservoir in the period between 1983 and 1986. Then, the piscivores were dominant (25.6%), followed by iliophagous (15.6%), omnivores (12.5%), insectivores (9.4%), herbivores (3.4%), planktivores (1.6%), lepidofages-insectivores (1.6%), and others (9.4%). Agostinho et al. (1999) in a 6-year study (1983 to 1989) of the Itaipu Reservoir, found similar results, with higher occurrences of omnivores and piscivores. Oliveira et al. (2005) found greater biomass of hake *Cynoscion* spp. (piscivores), detritivores, and omnivores in the Itaipu Reservoir. The differences between the trophic guilds of fishes in the present study compared to those of Oliveira et al. (2005), can be explained by differences in sampling methodology, as these authors used only gillnets in their studies. The results presented here are derived from landings of commercial fishing, where fish biomasses are best represented by the fact that fishermen pursue this activity with greater frequency. The monitoring of professional fisheries in the Itaipu reser-

voir began in 1985 and persists to this day, and it is of great importance for understanding the dynamics of fishes in the reservoir.

Agostinho et al. (1997a) characterized the structure of trophic guilds of fishes of the Paraná River, in which piscivores were more abundant and diverse. The authors emphasize that the dynamics of the environment is related to the diversity of species in trophic categories, as evidenced by the structure of the diversity of its abiotic component and by the biotic interrelationships governed by the hydrological cycle.

As the Itaipu Reservoir is an artificial damming of the Paraná River, it is expected that the structure of the fish community should have a strong influence of the hydrological regime of the river. The study mentioned above found greatest abundance of piscivores and iliophagous, both favored by the effect of the flood pulse, developing ideal areas that favor the increase of these stocks (reproduction and feeding). This effect may explain the large biomass of omnivores and piscivores recorded in this study, in which the riverine and transition zones showed large biomasses of omnivores, and piscivores were more dominant in the lacustrine zone.

13.4.4 Trophic Relationships (top-down and bottom-up) in the Itaipu Reservoir: Direct and Indirect Effects

The theory of trophic cascade in lakes and reservoirs is based on the fact that each trophic level of the food chain is inversely and directly related with trophic levels above or below, following two principles: the loss of energy between a trophic level and a higher one, and the disturbance in a trophic level brings consequences to the remaining trophic levels. The studies that have tested and confirmed this hypothesis in temperate lakes and reservoirs are numerous (Hrbáček et al. 1961; Shapiro et al. 1975; Shapiro and Wright 1984; Carpenter et al. 1985; Persson et al. 1988; Carpenter and Kitchell 1988; Mcqueen 1990; Power 1990; Brett and Goldman 1996; Brett and Goldman 1997; Hairston and Hairston 1997; Meijer et al. 1999; Jeppesen et al. 2000; Gulati 2001; Carpenter et al. 2001; Benndorf et al. 2002; Lathrop et al. 2002; Bell et al. 2003; Hansson et al. 2004; Borer et al. 2005; Mehner et al. 2005), unlike what happens in tropical lakes, where studies of trophic cascades are scarce (Quirós and Boveri 1999; Scasso et al. 2001; Hasan et al. 2001; Lazzaro et al. 2003; Rejas et al. 2005; Jeppesen et al. 2005).

The top-down effects in temperate environments are explained by Mcqueen (1990) and Lazzaro (1997), where relationships between trophic levels suffer negative effect of the presence of piscivores on the lower levels.

Lazzaro et al. (2003) investigated the effects of trophic cascades in dams of Pernambuco. The relationships that are well explained in temperate climate lakes and reservoirs were not so evident in tropical environments. The authors suggest that the state of the trophic guilds of fishes plays the main role in food webs in reservoirs of northeastern Brazil, where indirect effects between chlorophyll concentration and the densities of omnivores have a positive relationship, indicating that omnivores somehow contribute with some kind of pressure towards the development of chlorophyll-a. According Jeppesen et al. (2005), this is because the wealth of fish species is often higher in tropical and subtropical lakes. South America and Africa have a very rich freshwater fish fauna and many species of fishes show a partially overlapping niche, increasing the control of prey (Lazzaro 1997). This effect was also observed by Stein et al. (1995) in lakes in southern United States.

Fish communities in tropical and subtropical lakes are often dominated by omnivores, which have great feeding plasticity, consuming zooplankton, phytoplankton, periphyton, benthic macro invertebrates, and debris. According to Lazzaro et al. (2003), the piscivores are represented in few species and in small biomass and a greater biomass of small carnivores and omnivores generally governs the dynamics of the trophic chain.

Some species of omnivores are not controlled by the availability of food resources (zooplankton) and not even by the pressure of predation as they are bigger in size than their potential predators (Arcifa et al. 1995). The top-down control by piscivorous fishes is therefore weaker in subtropical/tropical lakes than in temperate lakes.

Roche and Rocha (2005) discussed the effect of the presence of planktivores in lakes and reservoirs in Brazil, highlighting the effects of predation, food types and feeding selectivity, effects of fries and fingerlings, nutrient availability, trophic state of the environment and hydrology.

Lazzaro (1987) notes that in most previous studies involving the impact of planktivorous fish the feeding behavior of the species was not determined and, consequently, the mechanisms that determine the feeding selectivity of the fishes and the use of resources were not well-understood. The author explains that fishes have great ability to change their pattern of feeding selectivity, and classifies fishes according to the way they feed: visual particulate, filtration, pumping, and filtration drag. In the case of the first two, several factors influence the success of predation, as prey size and light intensity, and species of young fish that feed by visual mode particles may switch to filter-feeding by pumping when they become adults. Lazzaro (1991) demonstrated this effect in laboratory experiments with a cichlid species, the *Geophagus brasiliensis* (cará). Roche et al. (2005) tested the feeding selectivity for the same species in experiments in mesocosms *in situ* in the Lobo-Broa Reservoir (SP). The authors found that the biomass of *Daphnia* sp decreased in treated fish, showing the pressure for food selectivity, confirming the laboratory studies by Lazzaro (1991).

Predation has an important effect as it controls the excess of prey available, allowing better survival of the remaining fishes on the limited food supply, especially when the reproduction rate of the prey is very high, such as tilapia (Odum 1983).

In systems where there are high fish densities, there may be loss of weight and animal death (Mcqueen 1990). The presence of a predator provides stability to the system, since, with predation, there is a reduction of the stock of prey, thus avoiding the lack and competition for food by the forage species. Paiva et al. (1994) conducted a study where the number of predator species interfered with the trophic dynamics in reservoirs of northeastern Brazil. They noted that the reservoirs in which there were two species of predators fish catching was high, while in reservoirs with less than two species of predators, competition among prey probably contributed to the decrease in catch.

Several authors suggest that the community structure and biomass of fresh water are regulated by predators (Hrbáček et al. 1961; Shapiro et al. 1975; Shapiro and Wright 1984; Carpenter et al. 1985; Persson et al. 1988). It can be said that an increase in piscivore biomass is associated to reduction of planktivore biomass, increase of large zooplankton biomass and reduction of phytoplankton (Carpenter et al. 1985; Mcqueen 1990; Meijer 1999; Gulati 2001). The interactions established by predation can promote the reduction of the planktivore biomass and these, associated with increased biomass of large zooplankton and the increase of algae consumers (grazing), reduce the phytoplankton biomass. Several authors (Shapiro and Wright, 1984; Vanni and Findlay 1990) have noted that predators are important to zooplankton alterations.

According to the trophic cascade hypothesis, the increase in piscivore (carnivore) biomass in a lake or reservoir causes the planktivorous fish biomass to decrease, increasing the zooplankton biomass and reducing phytoplanktonic biomass (Shapiro et al. 1975; Carpenter et al. 1985).

Lazzaro et al. (2003) point out that top-down effects in tropical environments are more complex than in temperate environments, as there are no species that are essentially zooplanktivorous but omnivores (such as tilapia), and the piscivores give way to general macro carnivores. The chlorophyll-a concentration increases with the omnivorous fish biomass and decreases with macro carnivore biomass. However, in this work, the chlorophyll-a concentration was not related to total fish biomass and to the macrozooplankton biomass. Interactions between fishes and chlorophyll concentration and between fish and zooplankton biomass were inversely related to the trophic state. The fish-phytoplankton regulation caused by complex omnivore interactions is present in the feeding behavior of various populations of consumers.

The results show that the Itaipu Reservoir presented top-down and bottom-up relationships, supporting the findings by Rejas et al. (2005) in experiments in a lake in Bolivia, with direct and indirect effects on the trophic cascade. The top-down effect was found only in the first trophic level and the biomass of piscivores exercised a control over omnivores and detritivores, and had no predatory effect on the benthivore and zooplanktivore biomasses, whose biomasses actually increased. This suggests that the piscivores may have an effect on the water quality of the reservoir, not positively, but negatively, since the indirect relations between the guilds consumed by predators have shown to have a controlling effect on both chlorophyll-a and cyanobacteria. The control effect of piscivores was also reported by Pelicici et al. (2005) on 31 reservoirs of the state of Paraná.

The effect of omnivores on the other trophic groups of fishes was also evaluated, since this group is composed largely of big fish (*Pimelodus* sp and *Pterodoras granulosus*, for example). This analysis indicates that the increase in omnivore biomass caused depletion of benthivore and detritivore biomass, contrary to what happened with the zooplanktivore, which had their biomass increased.

An important relationship studied was the one between detritivores and primary production in the reservoir. Although the results indicate that this group suffers a strong predation pressure by piscivores and omnivores, detritivores promote control over chlorophyll-a and cyanobacteria.

When the omnivore filter-feeders dominate the planktivorous fishes, the hypothesis "fishes versus trophic state of the lake" can no longer be valid because the growth stimulation by omnivores is intensified by the increased load of nutrients (Drenner et al. 1996). The systems dominated by omnivores show weak trophic links, owing to a combination of weakened mechanisms. Consequently, they are difficult to predict with the trophic cascades hypothesis. Among the mechanisms involved, Lazzaro et al. (2003) comment on the "intraguild predation" (IGP), which applies to omnivores that feed on herbivorous zooplankton and on their phytoplanktonic food and also ontogenetic omnivory (the same mechanism that occurs during the fish ontogeny from the juvenile phase to the adult).

The lack of zooplanktivore predation effect demonstrated in the statistical analysis also indicates damage to water quality, with positive effect related to the cyanobacteria. Studies by Abujanrra and Agostinho (2002) emphasize the great adaptability that zooplanktivorous species have owing to their gill system, as their gills are large, long, thin, and numerous. For instance, the filtration mechanism of *Hypophthalmus marginatus* is of the passive filter kind that consists in swimming with an open mouth and with extended operculum, and their diet is composed primarily of zooplankton. These results demonstrate the importance of omnivore and detritivore chains in tropical and subtropical aquatic environ-

ments. These results corroborate the work of Lazzaro (1997) and Lazzaro et al. (2003), which emphasize the effect of omnivores and the detritivore chains in these environments.

The only guild of fishes that showed some relationship with the macrozooplankton was the one composed by iliophagous, and the relations were positive and not negative as they occur in temperate ecosystems (Mcqueen et al. 1990; Carpenter and Kitchell 1993). These results suggest that the increase in iliophagous biomass causes an increase in herbivorous zooplankton communities, indicating that the pressure of fishes does not affect the zooplankton community, which is capable of consuming the phytoplankton, what appears to be a bottom-up effect.

The low pressure the fishes cause on zooplankton implies the dominance of small individuals in the zooplankton communities in tropical and subtropical lakes (Lazzaro 1997). The omnivorous copepods biomass usually dominates in oligomesotrophic systems, whereas microzooplankton prevails in more eutrophic systems. At higher temperatures, the daily fluctuations of the physical or chemical conditions or sudden environmental changes (due to heavy rain, for example) may affect the zooplankton community (increasing the number of protozoa and rotifers), but it has the ability to recover very quickly. The classic control of phytoplankton by macrozooplankton in temperate lakes is not as often seen in tropical lakes (Lazzaro 1997; Jeppesen et al. 2005; Rejas et al. 2005). This absence of predation pressure on zooplankton may represent an additional limitation on the difficulty of biomanipulation in tropical and subtropical lakes.

While studying mesocosms Baca and Drenner (1995) found that the predator causes a strong impact on the planktivore community, but the interactions of the trophic levels below these communities did not show a strong effect on the phytoplankton and zooplankton communities. The results described above can explain the increased biomass of the zooplankton community, with regard to the macrozooplankton analyses (cladocerans and copepods), in this study. The results show that there is no predatory pressure of fish on zooplankton. Studies in 31 reservoirs in the state of Paraná showed the same positive relationship between chlorophyll-a and macrozooplankton. According Lazzaro (1997), in tropical environments prey are not strictly zooplanktivorous, but omnivorous, having no direct effect on zooplankton community.

The macrozooplankton (cladocerans and copepods) showed a positive relationship with chlorophyll, indicating that the former had no control over the latter. These results corroborate the work by Lansac-Tôha et al. (2005) and Piana et al. (2005), held in reservoirs of Paraná, in which positive relationships were also found between zooplankton and chlorophyll-a. This type of relationship is opposite to what is commonly found in temperate lakes and reservoirs (Mcqueen, 1990; Carpenter and Kitchell 1993), indicating a bottom-up effect.

The last trophic level examined, confirming the bottom-up effect, was the chlorophyll–nutrient interaction, where increased concentrations of chlorophyll-a were positively related to the concentrations of total phosphorus. In temperate environments this ratio is positive (Mcqueen 1990; Carpenter and Kitchell 1993), and nutrient concentrations control chlorophyll-a concentrations.

Hambright et al. (1991) point out that a complicating factor for the functioning of the trophic cascade hypothesis is the assumption that all populations of planktivorous fish are susceptible to increased biomass of piscivores. Hambright (1994) also shows that the morphological characteristics (such as mouth opening of predators) and prey refuges are factors of extreme importance for the development of the trophic cascade hypothesis.

Indirect relationships indicate that omnivores, insectivores and detritivores control chlorophyll and cyanobacteria. These three groups of fish can be used to control the quality of water in the reservoir, and laboratory and *in situ* experiments may provide answers for the management of this environment. The iliophagous and zooplanktivorous fish showed positive relations with chlorophyll-a and cyanobacteria, respectively. These results indicate that both groups of fish somehow stimulated the development of primary productivity. Measures such as the encouraging of catchment of these species in both artisanal and sport fisheries would bring beneficial results in the control of water quality in the reservoir.

Insectivores and herbivores were the only groups of fish that were somehow related to the concentration of total phosphorus. Both showed negative relationships with phosphorus, indicating that an increase of the biomass of these causes a reduction in the total phosphorus concentration. These results imply that management of these species (increase of stock) may have a greater control of total phosphorus in the reservoir.

Persson (1997) compared the rate of excretion of phosphorus in zooplanktivorous fish, with estimates of internal and external loads in a eutrophic lake (Lake Finjasjon, Sweden). The experiments were performed in the laboratory using two prey species (one benthic and one pelagic), and the results were extrapolated to the entire lake, using the calculation of consumption of prey by the fish, based on field data on community structure, growth rate of excretion and diet of the fish. The phosphorus rate excreted by the fishes was on average 0.53 mg P/m²/d, which had a 110 % increase of external load and 42 % of internal load. Most of the phosphorus released by the fish is recycled within the water column, that is, more than 18 % of phosphorus released in the water comes from the benthic food, thus representing the transportation of phosphorus from the sediment to the water column. Phosphorus excreted by the fishes became available for phy-

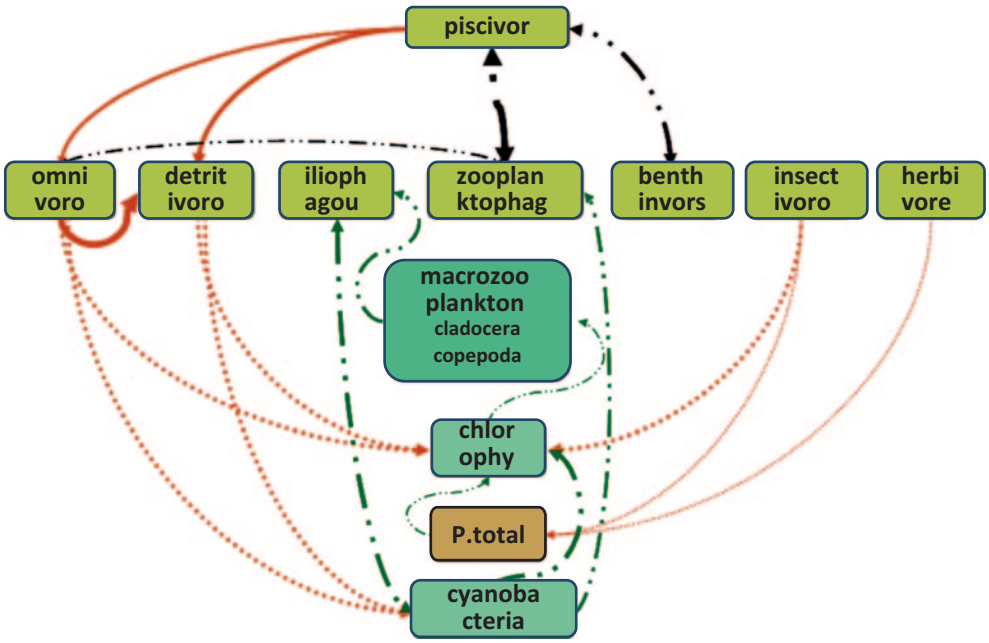

Fig. 13.9 Food web of the Itaipu Reservoir. The arrows directed downward indicate a top-down effect, the line and dot arrows indicate a bottom-up effect, dotted arrows indicate an indirect effect, the thickness of the arrows indicate the correlation coefficient of these relations and the colors indicate the different trophic levels (fishes, zooplankton, phytoplankton and nutrients)

toplankton, suggesting that the nutrient may constitute an important source for algae.

Fishes release phosphorus in the water directly through metabolic processes (excretion) and, indirectly owing to their habit of turning the sediment in search of food, making nutrients available in the water column (Persson 1997; Pereira and Ribeiro Filho 2004). Starling (1998) stresses that the importance of fish in maintaining the concentration of phosphorus of the water can be greater than that of allochthonous sources, primarily as a source of nutrients in the pelagic region. Brabrand et al. (1990) point out that the soluble phosphorus is the main form of phosphorus excreted by fish, and Starling (1998) demonstrated that tilapia are the fish that have the highest rate of excretion of soluble phosphorus in Lake Paranoá.

While analyzing the relations between one trophic level and another, we observed that the Itaipu Reservoir presents strong evidence of a bottom-up force, whose positive effects can be found throughout the reservoir. Only the analyses of the fish predation effect on fish showed negative relationships, indicating that there is a top-down effect. These results suggest that the Itaipu Reservoir presents both types of effect. While the bottom-up effect was observed in three trophic levels, the top-down effect was found only in one level. The food web is presented in Fig. 13.9 and shows the direct and indirect top-down and bottom-up effects in the Itaipu Reservoir.

It is important to stress that the Itaipu Reservoir, located in the subtropical region, receives large tributaries (rivers Paranapanema, Tietê, and Grande) from the state of São Paulo and is located in the tropical region. Does the Itaipu reservoir have a strong influence of tropical systems? Does the cascade reservoirs system upstream of the Itaipu Reservoir have an influence on the dynamics of the food web? Studies with this same approach, including other variables such as macrophytes biomass and predatory birds and benthic macro invertebrates, may help to elucidate this issue.

According Straškraba and Tundisi (2000), the food web of a reservoir is represented by several groups of organisms according to their lifestyles and feeding habits. The groups of organisms are mutually related to each other mainly by their feeding habits, by allelopathic reactions (by chemical compounds released by organisms), by the behavioral reactions and by the recycling of nutrients. The authors stress the importance of knowing aquatic organisms and the food web of a reservoir, in which the presence or absence of certain species and their food web serves as a long-term indicator of water quality.

13.4.5 Inference of Fish Yield

Predictive models to estimate the production and fish yield are commonly used in African and North American lakes and reservoirs (Henderson and Welcomme 1974; Meleck 1976; Oglesby 1977; Schleisinger and Regier 1982; Marshall 1984; Sass and Kitchell 2005).

Numerous independent variables can be used to predict indices that explain fishing yield in lakes and reservoirs, through biotic and abiotic variables (reservoir area, average depth, alkalinity, air temperature, water transparency, dissolved solids, morfoedaphic index—MEI, chlorophyll, and phytoplankton biomass, primary production, benthos, macrophytes, fish biomass) that can be tested in univariate and multivariate models.

According to the results found, the model predicts that increasing concentrations of cyanobacteria involves depletion of fish catches in the Itaipu Reservoir. The correlation coefficient explained 68 % ($p = 0.05$). Piana et al. (2005), in a study of 29 reservoirs of the state of Paraná, developed a multivariate model, in which fish biomass was explained by the chlorophyll-a and zooplankton variables. The authors emphasize that the bottom-up effect in these environments is explained by the positive relationship with chlorophyll-a and negative with zooplankton.

The inference of fish yield calculated by the equation of Meleck (1974) was 8.1 kg/ha/year and this result is similar to that obtained by Agostinho and Gomes (2005), who found an average of 7.9 kg/ha/year for the years 2000–2004, indicating that an analysis for the formulation of a specific model for the reservoir can reveal accurate predictions.

It is important to stress that these models provide a quick estimate, but the continued monitoring of professional and amateur fishing over a long period of time (as it is currently done by Itaipu) are of utmost importance for the understanding of fishing yield, as well as the dynamics of the structure of species of the reservoir.

The relationship between MEI and water transparency was verified by regression analysis. This relationship indicates that the increase in water transparency influences the depletion of MEI ($R = 0.687$, $p = < 0.001$, $F = 62.59$), and the relationship between chlorophyll-a and the MEI is inverse to water transparency ($R = 0.325$, $p = 0.005$, $F = 8.268$). The same behavior of relationships was also observed in Indian reservoirs (Hasan et al. 2001), in which water transparency had a negative effect and chlorophyll-a, positive. These relationships indicate that the analysis of the MEI and a series of fish production data can generate a predictive model of fishing yield for the reservoir. An analysis using the morphoedaphic index and catches may reveal a more accurate model for fishing yield. According to Marouelli et al. (1988), estimates on abundance and fishing yield are necessary as tools for solving problems related to fisheries management in reservoirs.

Another aspect to be considered is that all analyses of water quality variables were performed with data collected from the water surface. This may explain why the model created that showed in Fig. 13.9 regarding data from cyanobacteria. This group of algae is dominant in the superficial regions of lakes and reservoirs, and the action of winds is a determining factor for the appearance of blooms (Tundisi 1990).

The lack of detailed information on fish production prevented the creation of more efficient and powerful predictive models. This line of research is of great value, and good models that can infer the production and fishing yield in lakes and reservoirs are tools that can be used by the agencies responsible for aquatic resources management in Brazil.

13.5 Conclusions

Evaluating the results, it was possible to conclude that the trophic cascade hypothesis in the Itaipu Reservoir showed both top-down and bottom-up effects, and the negative effect of piscivores was seen only in the trophic level below, and the effect of the other levels were positive, featuring a stronger bottom-up force. The cycle of the food web seems to be explained by the omnivore and detritivore biomasses, an effect observed in tropical and subtropical environments, being of extreme importance in the (indirect) relationships, and determining the controlling forces of primary productivity in the reservoir. The limnological variables in the Itaipu Reservoir showed a pattern of spatial (horizontal) and temporal variations that is strongly dependent on the hydrological regime. The forms of nutrients influenced the development of primary productivity (as measured by chlorophyll-a), and while the TKN and total phosphorus had a positive effect, ammonia nitrogen and nitrate had a negative effect. The models created answer how these variables influence the concentration of chlorophyll-a. The negative effect of turbidity and suspended solids on water transparency was confirmed by means of linear regression analyses, and the generated models explain around 61 % of this effect at a high significance level.

The transition zone was the one with the highest concentrations of nutrients, higher chlorophyll concentration, higher density of cyanobacteria and zooplankton and a higher trophic degree, characterizing eutrophic conditions, but, on average, it was considered mesotrophic.

The average results of the trophic state indices indicate an oligotrophic status for the entire reservoir as well as for the riverine, transition, and lacustrine zones separately. It is possible to verify, during years of study, that the process of eutrophication of the reservoir is occurring slowly, but some high values found highlight larger inputs of nutrients.

The increase in primary productivity, expressed by chlorophyll-a, was explained by increased levels of total phosphorus in which the models were significant and responded for more than 40 % of this ratio.

Cyanobacteria were dominant in the Itaipu Reservoir, and their highest values were obtained in the transition zone. Increasing concentrations of chlorophyll-a were positive and significantly related to the greater density of cyanobacteria. Cyanobacteria also suffered the influences of abiotic variables such as water transparency, turbidity, suspended solids, and TKN, and the latter had a negative effect on the development of algae. The model created explains 57 % of these relationships.

The fishes that exercised the greatest control over cyanobacteria were omnivores and detritivores. The models explain about 88 % of the relationship pressure of these groups of fish on these algae. Zooplanktivorous fishes did not pres-

ent any controlling effect on the densities of zooplankton, and their development was positively related to cyanobacteria, indicating growth of the latter. The *Prochilodus lineatus* was the only species to compose the iliophagous group, having a positive effect regarding chlorophyll-a, and the concentrations of the latter increased with the increase of iliophagous fish biomass.

Omnivores and detritivores were the trophic guild groups that showed a controlling effect on the cyanobacteria and chlorophyll-a, indicating that when these groups of fish increase, they reduce primary productivity in the reservoir. The piscivores may be presenting a negative effect on water quality of the Itaipu Reservoir, in which the control effect is exercised by the biomass of omnivores and detritivores.

The fish yield was estimated by the relation with cyanobacteria concentration, and this was the variable that best explained this prediction, in 68 %. The use of the MEI, with the recorded catch data, can generate predictive models that estimate the fishing yield in the Itaipu Reservoir. The relations of MEI with chlorophyll-a and water transparency indicate that this index may be a good predicting factor for future fish captures.

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Phytoplankton Assemblages as an Indicator of Water Quality in Seven Temperate Estuarine Lakes in South-East Australia

14

Dongyan Liu, R. J. Morrison and R. J. West

Abstract

Phytoplankton species diversity and their ecological characteristics in seven coastal estuaries of different eutrophication status in southeast Australia were described. Seasonal patterns in physical and chemical properties of the waters were assessed over 2 years, along with chlorophyll a data and phytoplankton numbers and diversity. It was found that the phytoplankton species composition and biomass pattern reflected the characteristics of temperature, salinity, nutrients, and habitat in the studied estuaries. A total of 145 species were identified in the different lakes with Diatom and Dinoflagellete species being the main contributors to phytoplankton diversity. Seasonal patterns of phytoplankton assemblages showed that maxima occurred in winter or spring, being mainly affected by temperature and nutrient availability. The eutrophic indicative signals of the phytoplankton species distributions appear to be diminished by the presence of large seagrass beds and extensive macroalgae growth.

Keywords

Eutrophication · Estuaries · Phytoplankton

14.1 Introduction

There are more than 130 estuaries in New South Wales (NSW), Australia, with about 50% of them considered as Intermittently Closed and Open Lakes or Lagoons (ICOLLs) (Roy et al. 2001). These ICOLLs range from small mostly closed lagoons to large open lakes and are very important catchments for local (recreation) and fish nursery. Over recent decades, urbanization, habitat modification, population growth, and agriculture have significantly influenced the ecosystems of these estuaries, e.g., about 17% of mangroves and 21% of saltmarshes have been lost since European settlement (Turner et al. 2004). Moreover, the water quality of estuaries near the large population centers has been deteriorating owing to rising nutrient levels and other chemical pollutants (Scanes et al. 2007).

Phytoplankton can be greatly impacted by environmental change, especially increases in nutrients, and microalgal blooms have been widely observed in Australian estuaries and reported by scientists and governments over the past two decades (e.g., Ajani et al. 2001, 2002). Little information is available, however, on phytoplankton assemblages in the estuaries of NSW and such information has therefore not been commonly used in the assessment of water quality. Thus, a comprehensive understanding of the phytoplankton communities including species composition, biomass and seasonal patterns, is urgently required for improving the environmental management of the estuaries of NSW.

In contrast to coastal rivers and embayments, which have free exchange with ocean waters, only limited research

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has been carried out on the phytoplankton assemblages in ICOLLs. Phytoplankton biomass in ICOLLs can be decreased by the dilution of seawater when the lake entrance is open to the sea, high grazing pressure and even nutrient competition with seagrass, macroalgae, or saltmarsh. Consequently, these factors may also reduce the usefulness of phytoplankton as an indicator of the "environmental health" of these systems (Perissinotto et al. 2002; Cummins et al. 2004; Gobler et al. 2005). A comparative study is therefore required to assess the usefulness of phytoplankton as an indicator of environmental change. In this study, seven ICOLLs in southern NSW were chosen to explore the relationship between a suite of environmental factors and the phytoplankton assemblages. Phytoplankton species diversity, biomass, and seasonal patterns were studied and the possible role of phytoplankton as an indicator of water quality was evaluated in a range of ICOLLs characterized by different physical and chemical conditions.

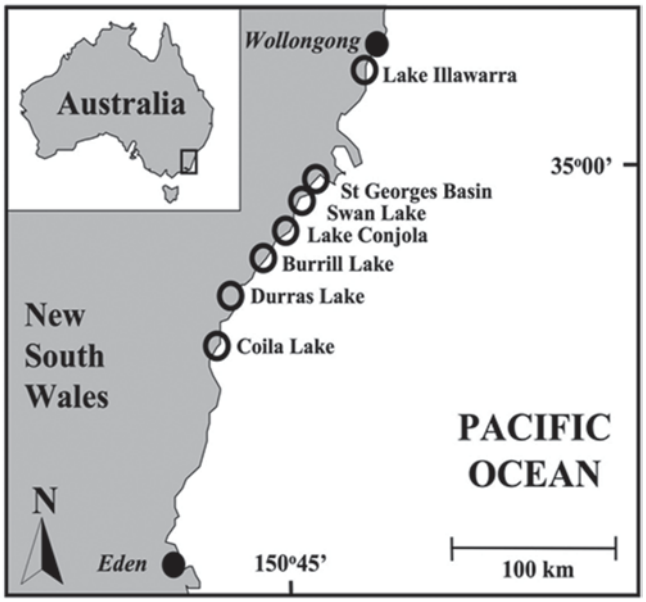

Fig. 14.1 The locations of seven estuaries studied in NSW Australia

14.2 Materials and Methods

14.2.1 Studied Estuaries and Sampling Methods

Seven representative ICOLLs, Lake Illawarra, Burrill Lake, Swan Lake, St. Georges Basin, Durras Lake, Conjola Lake, and Coila Lake, which were characterized by different degrees of urban development in their catchments, as well as physical, chemical and biological conditions, were chosen for investigating the relationship between environmental factors and phytoplankton assemblages (Fig. 14.1 and Table 14.1).

Lake Illawarra and St. Georges Basin are relatively large coastal estuaries with a wide shallow basin and high catchment populations (ABS 2003), Durras Lake, Burrill Lake, and Coila Lake are characterized by a relatively large area but low population density; Conjola Lake and Swan Lake are small and have very low human activity in their catchments. More information on these lakes is available at: http://www.environment.nsw.gov.au/estuaries/index.htm.

Five field observations to examine seasonal patterns were carried out in the seven lakes in June 2005 (winter), October 2005 (spring), June 2006 (winter), December 2006 (summer), and April 2007 (autumn), respectively.

Three sampling sites were chosen in each estuary to provide a representation of the different geographical environments (main body of lake, seawater entrance to the lake and freshwater entrance to the lake) and each site was located during the project using a GPS (Table 14.2). Full details are available in Liu (2008).

Physical parameters including salinity, temperature, turbidity, and pH were measured *in situ* at a depth of approximately 1 m using YSI 6820 (USA) multiprobe water quality recorder. Surface seawater samples were collected for Chl a analysis; additional samples were filtered on site through 0.45 μm Whatman GF/F filters for nutrient analysis. Phytoplankton samples were collected using a 20 μm net by towing at a speed of 2 knots for 2 min at a depth of about 0.3–0.6 m along a horizontal transect at each sampling site, which had been established using a GPS. A further 1 L of concentrated lake water was collected at each sampling site, decanted into a plastic bottle and preserved using formaldehyde (5% final concentration) for species composition analysis.

14.2.2 Laboratory Analyses

Nutrient samples brought back to the laboratory were stored frozen before measurement. Samples were thawed on the day of analysis. Dissolved inorganic nutrients, including nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), were determined with a LACHAT Quik-chem 8000 nutrient autoanalyzer using standard protocols (APHA 1998). The limits of detection were 0.14 μM for NO_3^-, NO_2^-, and NH_4^+, 0.01 μM for PO_4^{3-}, and 1.24 μM for DSi, respectively. Appropriate quality control procedures were emplaced involving the use of standard samples, blanks, and replicates.

Chl a concentrations was measured and calculated using the nonacidification spectrophotometric method (Jeffrey

Table 14.1 General information for the studied estuaries. (Data from NSW Office of Environment and Heritage)

Items	Catchment area (km^2)	Waterway area (km^2)	Entrance characteristics	Resident population (2001 Census)	Seagrassarea (km^2)
Lake Illawarra	270	36.3	Mostly open and untrained	~90,000	5.142
St. Georges Basin	32	11	Intermittently or mechanically opened and untrained	11,880	8.538
Swan Lake	34	4.5	Intermittently open and untrained	580	0.587
Burrill Lake	78	4.1	Generally open and untrained	1,410	0.508
Conjola Lake	145	5.9	Mostly open and untrained	940	0.527
Durras Lake	55	3.5	Intermittently open and untrained	330	0.509
Coila Lake	48	6.3	Closed except when artificially opened	1,050	1.86

and Humphrey 1975). Chl a was extracted from filters using 90 % acetone in the dark for 24 h at 4 °C, cleaned up by centrifugation, and then measured using a spectrometer (Shimadzu UV 1700). Phytoplankton species were identified under a microscope (Olympus, CKX31) in the laboratory. Taxonomy and nomenclature were assessed by reference to Fenner et al. (1976), Hasle (1976), Hasle and Syvertsen (1997).

14.2.3 Data Analysis

Data analysis included species similarity analysis on the species composition data (PRIMER Version 5), and multilinear regression analyses between the phytoplankton biomass and environmental factors (SPSS 13.0).

Table 14.2 The GPS positions of sampling sites in the seven lakes

	Site 1	Site 2	Site 3
Lake Illawarra	34.31°S	34.31°S	34.30°S
	150.51°E	150.50°E	150.50°E
Burrill Lake	35.38°S	35.37°S	35.35°S
	150.44°E	150.43°E	150.44°E
St. Georges Basin	35.15°S	35.12°S	35.10°S
	150.59°E	150.60°E	150.57°E
Swan Lake	35.19°S	35.18°S	35.17°S
	150.56°E	150.55°E	150.54°E
Durras Lake	35.65°S	35.64°S	35.62°S
	150.29°E	150.27°E	150.27°E
Conjola Lake	35.26°S	35.25°S	35.23°S
	150.48°E	150.45°E	150.45°E
Coila Lake	36.05°S	36.03°S	36.01°S
	150.14°E	150.13°E	150.11°E

14.3 Results

14.3.1 Spatial Variation of Physical Environmental Factors in the Studied Estuaries

During the sampling period, the studied estuaries displayed typical warm-temperate waters characteristics (Fig. 14.2a).

Water temperature did not show any obvious geographical differences between lakes, average water temperatures were about 19.4 °C in spring (October), 23.3 °C in summer (December), 20.3 °C in autumn (April), and 13.2 °C in winter (June) in this region.

Salinity exhibited some differences in the studied estuaries (Fig. 14.2b). Lakes can be classified into three types based on the range in salinity, namely mesohaline (5–18 psu), polyhaline (18–30 psu), and euhaline (30–40 psu). Swan Lake was found to be mesohaline and ranged from 12 to 23 psu with a mean value of 17.1 psu; Conjola Lake, Coila Lake, and Lake Illawarra are defined as polyhaline with mean values of 19.0, 27.1, and 26.7 psu, respectively; St. Georges Basin, Durras Lake, and Burrill Lake can be classified as euhaline because salinity ranged from 30 to 35 psu on most occasions.

The mean pH in most of the studied estuaries varied within the normal range for coastal water bodies (pH = 7.5–8.0), except for Swan Lake (Fig. 14.2c). High pHs were observed in Swan Lake with a mean of 8.6 during the sampling period. High pH values (about 9.0) have been previously noted for this lake (Sullivan 2003). Turbidity also showed a gradient in the studied estuaries during the sampling period (Fig. 14.2d). The highest turbidities generally occurred in Lake Illawarra, where most values were greater than 5.0 NTU. Low turbidities were found in Swan Lake and Conjola Lake with most values below 2 NTU. Other lakes (St. Georges Basin, Bur-

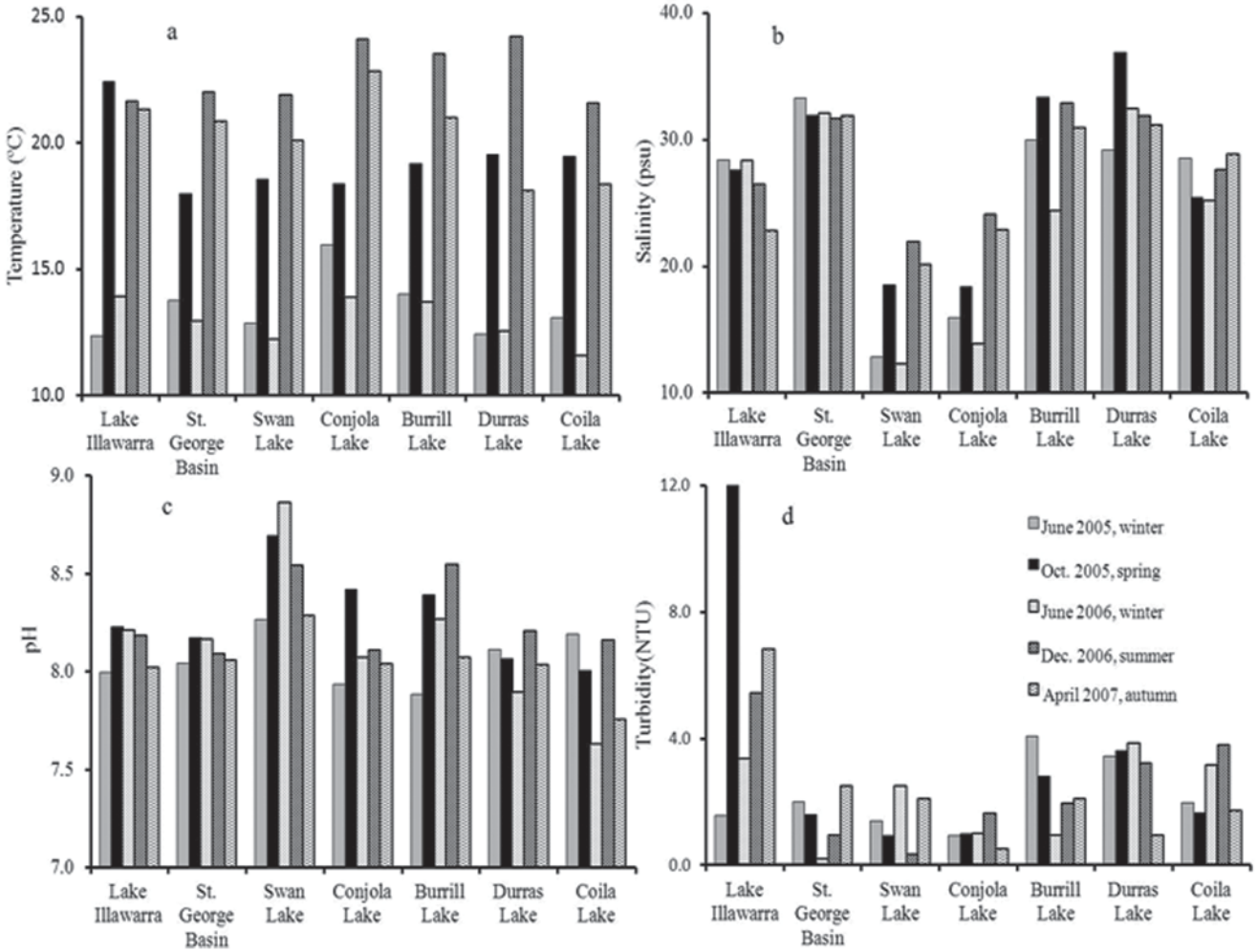

Fig. 14.2 Spatial variations of physical parameters in the studied estuaries during the sampling period

rill Lake, Durras Lake, and Coila Lake) displayed a range of turbidities between 2 and 4 NTU.

14.3.2 Spatial Variation of Chemical Environmental Factors in the Studied Estuaries

During the sampling period, the patterns and concentrations of nutrients displayed distinct differences in both spatial and temporal scales (Fig. 14.3).

Specific characteristics were observed in Lake Illawarra, Coila Lake, and Swan Lake. Lake Illawarra displayed the highest DIP concentrations but moderate levels of DIN compared to the other lakes (Fig. 14.3a, b); it was thus characterized by a significant N-limitation (Fig. 14.3d). In contrast, Coila Lake was characterized by very low DIP concentrations but the highest DIN concentrations (Fig. 14.3a, b), indicating possible P-limitation (Fig. 14.3d). Swan Lake displayed the lowest DIN and DIP concentrations of all of the studied lakes. For other lakes, most of the DIN concentrations were no more than 2 μM and DIP concentrations were usually lower than 0.1 μM (Fig. 14.3a, b) and an alternation of N-limiting and P-limiting conditions occurred in these estuaries during the sampling period (Fig. 14.3d).

DSi concentrations were high in all of the studied estuaries (Fig. 14.3c). These high values for DSi probably reflect the fact that all the catchments of the studied lakes are dominated by quartz sandstones (Branagan and Packham 2000). The mean concentrations of DSi showed a gradient from St. Georges Basin (14.5 μM) > Coila Lake (13.7 μM) > Conjola Lake (13.5 μM) > Durras Lake (11.6 μM) > Lake Illawarra (11 μM) > Burrill Lake (9.37 μM) > Swan Lake (9.31 μM). DIN:DSi values were mostly below the Redfield (1958) ratio (DIN:DSi = 1:1) in the studied estuaries (Fig. 14.3d, e). Overall, these values suggest a very low probability that Si was limiting phytoplankton growth in any of the studied estuaries.

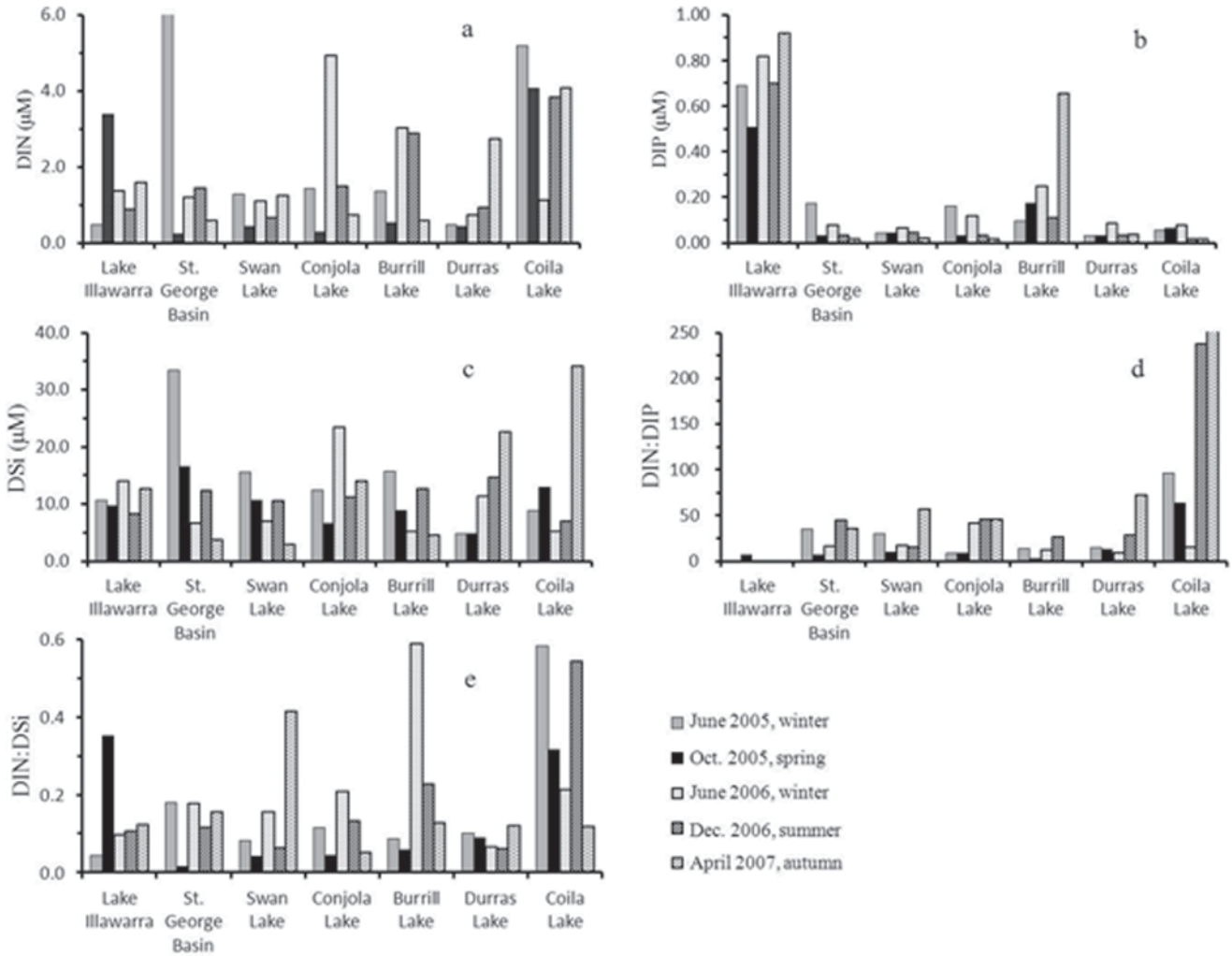

Fig. 14.3 Spatial variations of nutrients in the studied estuaries during the sampling period

14.3.3 Spatial Variation of Phytoplankton Assemblages

In this study, 145 phytoplankton species were identified. These cover five groups, Cyanophyta, Chlorophyta, Chromophyta, Diatoms, and Pyrrophyta. The main contributors to the phytoplankton assemblages were diatoms with 95 species, followed by 34 Pyrrophyta species, 8 Cyanophyta species, 3 Chlorophyta, and 2 Chromophyta species (Table 14.3).

Temperate species dominated the phytoplankton assemblages, but, a few tropical species were identified (e.g., *Hemidiscus hardmannianus*, *Prorocentrum mexicanum*), and some *Protoperidinium* species with a preference for temperate conditions (Hasle and Syvertsen 1997) were often observed (Table 14.3). The ecological preference of the phytoplankton species reflected the temperate to warm climatic regime of these estuaries.

Owing to the effect of shallow water (the average water depth is usually no more than about 3 m), and the large-scale distribution of seagrass and macroalgae in these coastal lakes, phytoplankton assemblages displayed a combination of euplanktonic (e.g., *Coscinodiscus centralis*), tychoplanktonic (e.g., *Pleurosigma normanii*), epiphytic (e.g., *Amphora hyalina*), and periphytic species (e.g., *Achnanthes longipes*) (Hasle and Syvertsen 1997; Guo and Qian 2003). Moreover, the different proportions of freshwater species (e.g., *Tabellaria fenestrata*), brackish species (e.g., *Amphora hyalina*) and marine species (e.g., *Lauderia borealis*) in the phytoplankton assemblages were an indication of the variable salinity of these estuaries.

Species similarity analyses based on phytoplankton composition indicated that there were consistent differences between the lakes (Fig. 14.4).

St. Georges Basin and Durras Lake had the highest similarity in species composition, followed by Coila Lake, and then Lake Illawarra. However, lower species similarities were found for Burrill Lake, Conjola Lake, and Swan Lake. High concentrations of dinoflagellates in Burrill Lake and

Table 14.3 Phytoplankton species composition in studied estuaries during the sampling period

Location species	Illawarra Lake	Burrill Lake	St. Georges Basin	Swan Lake	Durras Lake	Conjola Lake	Coila Lake
Achnanthes longipes C. Agardh ● BM	+	+	+	+	+	+	+
Akashiwo sanguinea K. Hirasaka [a] M, R, T	+	+	+	−	+	+	+
Alexandrium tamarense E. Balech [a] BM, R, T	+	+	+	−	+	−	+
Amphora hyalina Kützing ● BM	−	−	+	+	+	+	+
Aphanocapsa sp. Δ B	−	−	−	+	−	−	
Asterionella japonica Cleve ● M, R	+	−	+	−	−	−	+
Ardissonia crystallina (Agardh) Grunow ● FB	−	−	−	+	−	−	
Bacillaria paradoxa J.F. Gmelin ● M, R	+	+	+	+	+	+	+
Biddulphia pulchella S.F. Gray ● M	−	−	+	−	+	+	−
Cerataulina bicornis (Ehrenberg) Hasle ● M, R	−	+	+	−	+	+	−
Cerataulina pelagica (Cleve) Hendey ● M	+	−	−	−	−	−	−
Ceratium furca Ehrenberg [a] M, R	+	+	+	+	+	+	+
Ceratium fusus Ehrenberg [a] M, R	+	+	+	+	+	+	+
Ceratium macroceros Ehrenberg [a] M	+	+	+	−	+	+	+
Ceratium tripos Nitzsch [a] M	+	+	+	+	+	+	+
Chaetoceros affinis Lauder ● M, R	−	−	−	−	+	+	+
Chaetoceros anastomosans Grunow ● M	+	+	+	−	+	−	+
Chaetoceros brevis Schütt ● M	+	+	+	−	+	−	+
Chaetoceros compressus Lauder ● M	+	+	+	−	+	−	+
Chaetoceros constrictus Gran ● M	+	+	+	−	+	−	+
Chaetoceros costatus Pavillard ● M	+	−	+	−	+	−	+
Chaetoceros curvisetus Cleve ● M, R	+	+	+	+	+	+	+
Chaetoceros danicus Cleve ● M	−	−	−	−	+	+	+
Chaetoceros debilis Cleve ● M, R	+	−	+	−	+	+	+
Chaetoceros decipiens Cleve ● M	+	+	+	−	−	−	+
Chaetoceros didymus Ehrenberg ● M	+	+	+	−	+	−	+
Chaetoceros laciniosus Schütt ● M	−	−	−	−	+	+	+
Chaetoceros lauderi Ralfs in Lauder ● M	+	+	−	−	−	−	−
Chaetoceros lorenzianus Grunow ● M, R.	+	+	+	+	+	+	+
Chaetoceros peruvianus Brightwell ● M	−	−	−	−	+	+	+
Chaetoceros pseudocurvisetus Mangin ● M	+	+	+	+	+	+	+
Chaetoceros socialis Lauder ● M, R	+	−	−	−	−	−	−
Chaetoceros similis Cleve ● M	−	+	−	−	−	−	−
Chaetoceros teres Cleve ● M	+	−	+	−	+	+	+
Chlamydomonas reginae Ettl & Green ♣ BM	+	+	+	+	+	+	+
Chroococcus sp. Δ FB	−	−	−	+	−	−	−
Climacospheniamoniligera Ehrenberg ● FB	−	−	−	+	−	−	−
Cocconeis placentula Ehrenberg ● FB	+	+	+	+	+	+	+
Coelosphaerium sp. Δ FB	−	−	−	+	−	−	−
Coelastrum sp. ♣ FB, R	+	+	−	−	−	+	−
Copmhosphaeria sp. Δ FB	−	−	−	+	−	−	−
Coscinodiscus asteromphalus Ehrenberg ● M, R	+	−	−	−	−	−	−
Coscinodiscus centralis Ehrenberg ● M, R	+	+	+	+	+	−	+
Coscinidiscus concinnus W. Smith ● M, R	+	+	+	+	+	+	+
Coscinodiscus radiatus Ehrenberg ● M	+	+	+	−	+	+	+
Coscinodiscus sp. ● M	+	+	+	−	+	+	+
Cylindrotheca closterium (Ehrenberg) Lewin & Reimann ● M, R	+	+	+	+	+	+	+
Diatomahyalina Kützing ● B	+	+	+	+	+	+	+
Dictyocha fibula Ehrenberg ♠ M	+	+	+	−	+	+	−
Dinophysis caudata Saville-Kent [a] M, R, T	−	+	−	−	+	−	−
Dinophysis dens Pavillard [a] M	+	+	+	−	+	+	+
Dinophysis diegensis Kofoid [a] M	+	+	+	+	+	+	+
Dinophysis fortii Pavillard [a] M, R, T	−	+	+	−	−	−	−

Table 14.3 (continued)

Location species	Illawarra Lake	Burrill Lake	St. Georges Basin	Swan Lake	Durras Lake	Conjola Lake	Coila Lake
Dinophysis homunculus Stein [a] M	+	+	+	−	+	−	+
Dinophysis ovum Schütt [a] M	+	+	+	−	+	+	+
Diploneis splendida Cleve ● B	+	+	+	−	+	+	+
Ditylum brightwellii Grunow ● M, R	+	−	−	−	−	+	−
Donkinia recta (Donkin) Grunow ● B	−	+	+	+	+	+	+
Eucampia zodiacus Ehrenberg ● M, R	+	−	+	−	+	−	+
Fragilariopsis oceanica Hasle ● B	+	+	−	−	−	−	+
Fragilariopsis doliolus Medlin & Sims ● B	+	+	+	−	+	+	+
Gonyaulax monacantha Pavillard [a] M, R	+	−	+	−	+	+	+
Gonyaulax polygramma Stein [a] M, R,	−	+	+	−	+	+	+
Gonyaulax spinifera Diesing [a] M, R	+	+	+	−	+	+	+
Guinardia delicatula (Cleve) Hasle ● M	+	+	+	+	+	+	+
Guinardia flaccida Castracane ● M, R	+	−	+	−	+	−	+
Guinardia striata Hasle ● M, R	+	+	+	−	+	−	+
Gymnodinium mikimotoi Miyake & Kominami ex Oda [a] M, R, T	+	−	+	−	+	−	+
Gymnodinium sp.[a] M	+	−	−	−	+	−	−
Gyrosigma fascicola (Ehrenberg) Cleve ● B	+	−	−	+	+	+	+
Gyrosigma baltcum (Ehrenberg) Cleve ● B	−	−	−	+	−	+	+
Hasleawawrikae (Husedt) Simonsen ● B	+	−	+	−	+	+	+
Hemiaulus hauckii ● M	−	+	−	−	−	+	−
Hemidiscus hardmannianus (Greville) Mann ● M	−	−	+	−	+	−	−
Katodinium glaucum (Lebour) Loeblich III [a] BM	+	−	+	+	+	+	+
Lauderia borealis Gran ● M	+	+	+	−	−	−	+
Leptocylindrus danicus Cleve ● M, R	+	+	+	−	+	+	+
Leptocylindrus mediterranneus Hasle ● M	+	+	+	−	+	−	+
Leptocylindrus minimus Gran ● M, R	+	−	+	−	+	−	+
Licmophora abbreviate C. Agardh ● B	+	−	+	+	+	+	+
Licmophora flabellata C. Agardh ● B	+	+	+	+	+	+	+
Lithodesmium undulatum Ehrenberg ● M	+	+	+	−	+	−	+
Masto gloia minuta ● B	+	+	+	+	+	+	+
Melosira hyperborean Grunow ● M	+	+	+	−	+	−	+
Melosira jüergensi C. Agardh ● M	+	+	+	−	+	−	+
Merismopedia glauca Ehrenberg Δ B	−	−	−	+	−	−	−
Mesocena polymorpha Lemmerman ♠ M	−	+	+	−	−	−	−
Navicula cancellata Donkin ● B	+	+	+	−	+	+	−
Navicula directa (W. Smith) Ralfs ● B	+	+	+	−	+	−	+
Navicula distans (W. Smith) Ralfs ● B	+	+	+	−	+	−	+
Navicula membranacea Cleve ● B, R	+	+	+	+	+	+	+
Navicula schroeteri F. Meister ● B	+	+	+	+	+	+	−
Nitzschia longissima Ralfs ● M, R	+	+	−	+	+	+	−
Nitzschia longissima var. *reversa* Grunow ● M	+	+	+	+	+	+	−
Noctiluca scintillans (Macartney) Kofoid et Swezy [a] M, R	+	+	+	−	+	−	−
Odontella obtusa Kützing ● M	+	+	+	−	+	−	+
Odontella reticulata (Roper) De Toni ● M	−	+	−	−	−	−	−
Phaeodactylum tricornutum Bohlin ● B	+	−	+	+	−	−	−
Phalacroma rotundatum Kofoid & Michener [a] M	−	+	−	−	−	−	−
Pinnularia acrosphaeria (Brébisson) W. Smith ● FB	−	−	−	+	−	−	−
Pleurosigma directum Grunow ● B	+	+	+	−	+	+	+
Pleurosigma intermedium W. Smith ● B	+	+	+	+	+	+	+
Pleurosigma rectum Donkin ● B	−	+	−	−	+	+	−
Pleurosigma normanii Ralfs ● B	+	+	+	+	+	+	+
Prorocentrum gracile Schütt [a] M	+	+	+	+	+	+	+

Table 14.3 (continued)

Location species	Illawarra Lake	Burrill Lake	St. Georges Basin	Swan Lake	Durras Lake	Conjola Lake	Coila Lake
Prorocetrum lima (Ehrenberg) Dodge [a] M, R, T	+	+	+	−	+	+	+
Prorocentrum mexicanum Tafall [a] M, R, T	−	+	+	−	−	−	−
Prorocentrum micans Ehrenberg [a] M, R	+	+	+	−	+	−	+
Prorocentrum minimum (Pavillard) Schiller [a] BM, R, T	+	+	+	−	+	−	+
Protoperidinium conicum (Gran) Balech[a] M	+	+	−	−	−	−	+
Protoperidinium depressum (Bailey) Balech[a] M	+	+	+	−	+	−	−
Protoperidinium grande (Kofoid) Balech[a] M	+	+	+	−	+	+	−
Protoperidinium pallidum (Ostenfeld) Balech[a] M	+	+	+	+	+	−	+
Protoperidinium pentagonum (Gran) Balech [a] M	+	+	+	+	−	−	−
Protoperidinium sp.[a] M	−	+	−	−	−	+	+
Protoperidinium steinii (Jørgensen) Balech[a] M	+	+	+	+	+	+	+
Protoperidinium pyriforme (Paulsen) Balech[a] M	+	+	−	+	−	−	−
Pseudo-nitzschia delicatissima (Cleve) Heiden ● B, R	+	+	−	−	−	−	−
Pseudo-nitzschia granii Hasle ● B	−	−	+	−	+	+	+
Pseudo-nitzschia subpacifica Hasle ● B	−	−	+	−	+	+	+
Pseudo-nitzschia prolongatoides Hasle ● B	+	+	+	−	+	+	+
Pseudo-nitzschia pungens Hasle ● B, R	+	+	+	+	+	+	+
Pseudo-nitzschia seriata H. Peragallo ● B	+	+	−	−	−	−	+
Pseudo-nitzschia sp. ● B	+	+	+	+	+	+	+
Pyrophacus steinii (Schiller) Wall & Dale [a] M	+	+	+	−	+	−	+
Rhabdonema adriaticum Kützing ● BM	−	−	−	+	−	−	−
Probosciaalata (Brightwell) Sündstrom ● M	−	+	+	+	−	+	−
Rhizosolenia setigera Brightwell ● M, R	+	+	+	−	−	+	+
Scrippsiella trochoidea (Stein) Balech ex Loeblich III [a] B, R	+	+	+	+	+	+	+
Skeletonema costatum (Greville) Cleve ● B, R	+	+	+	−	+	+	+
Staurastrum johnsonii West & G.S. West ♣ FB	−	−	−	+	−	+	−
Stephanopyxis turris Ralfs in Pritchard ● BM	−	−	−	+	−	+	−
Striatella unipunctata (Lyngbye) C. Agardh ● M	−	+	+	+	+	+	+
Synechocystis sp. Δ FB	−	−	−	+	−	-	−
Tabellaria fenestrata (Lyngbye) Kützing ● FB	+	−	−	+	+	−	−
Thalassionema frauenfeldii (Grunow) Hallegraeff ● M, R	+	+	+	+	+	+	+
Thalassionema nitzschioides (Grunow) Mereschkowsky ● M, R	+	+	+	+	−	+	+
Thalassiosira decipiens (Grunow) E.G. Jørgensen ● M	+	+	+	−	+	−	+
Thalassiosira hyalina (Grunow) Gran ● M	+	+	+	−	+	−	+
Thalassiosira rotula Meunier ● M, R	+	+	+	−	+	+	+
Thalassiosira subtilis (Ostenfeld) Gran ● M	+	−	+	+	+	+	+
Trichoclesmium erythraeum Δ M, R	+	+	+	+	+	+	+
Spirulina sp. Δ B	−	−	−	+	+	−	−

● Diatom, Δ Cyanophyta, ♣ a Chlorophyta, ♠ Chromophyta, [a] Dinoflagellate, + Present, − Absent, FB Freshwater to Brackish species, B Brackish species, BM Brackish to Marine species, M Marine species, R Red tide species, T Toxic species

low numbers in Conjola and Swan Lake were the main factors leading to these differences. The presence of Cyanophyta species was also important in differentiating the phytoplankton assemblages of Swan Lake from other lakes.

Spatial trends in Chl a concentrations in the studied estuaries were also evident (Fig. 14.5). The highest biomasses were observed in Lake Illawarra where Chl a concentrations ranged from 1.21 to 9.25 μg/L with a mean value of 5.36 μg/L during the sampling period; the lowest biomasses were found in Swan Lake with a Chl a range of 0.19–1.33 μg/L and a mean of 0.69 μg/L (Fig. 14.5). The annual average biomass displayed a spatial trend of Lake Illawarra > St. George Basin > Durras Lake > Burrill Lake > Coila Lake > Conjola Lake > Swan Lake.

Seasonal patterns of Chl a concentrations in the studied estuaries were not obvious during the sampling period (Fig. 14.5), which is reasonable, considering the warm temperate regime in the region. Previous studies have indicated that the seasonal patterns of phytoplankton assemblages were mainly determined by temperature and nutrient availability, cold temperate waters tend to show one peak in summer or two peaks in spring and summer, but warm waters

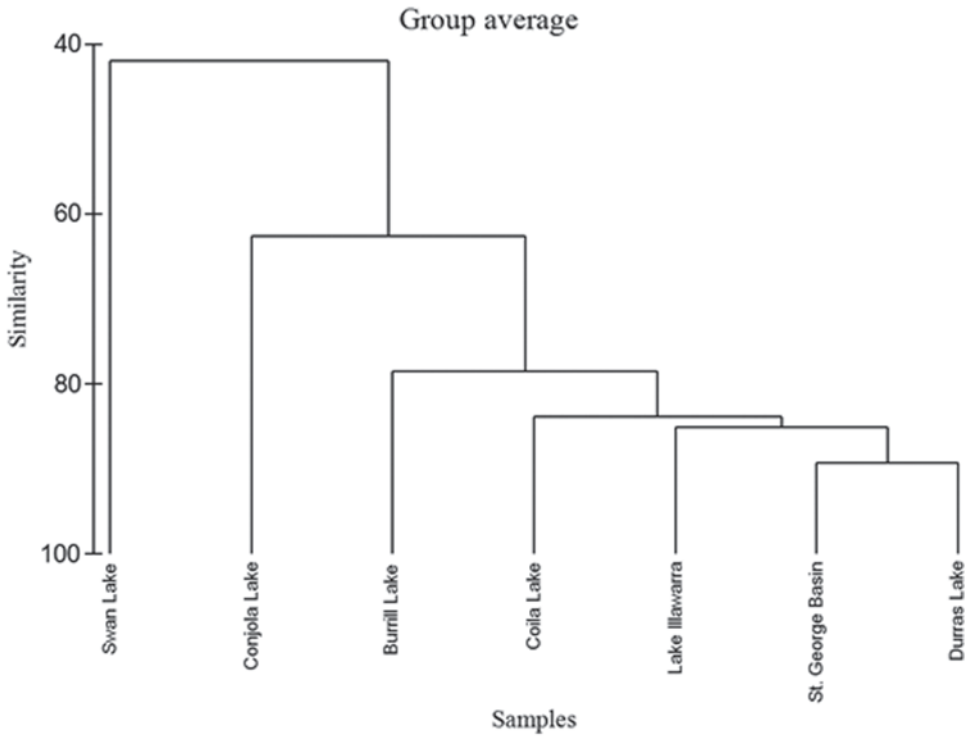

Fig. 14.4 The similarity of phytoplankton species composition in the studied estuaries

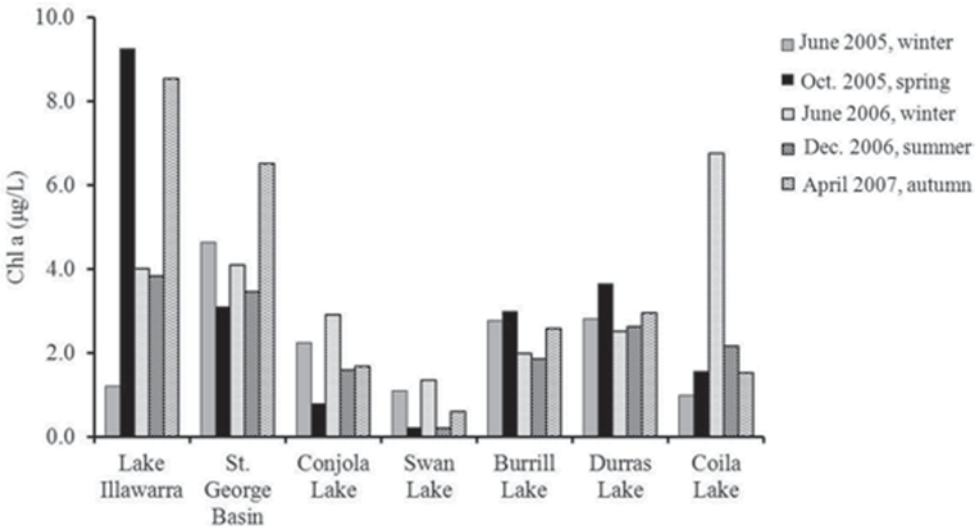

Fig. 14.5 Spatial variations of Chl a concentrations in the studied estuaries during the sampling period

usually show no strong seasonal peak (Anderson et al. 1994; Domingues et al. 2005).

14.4 Discussion

Based on the environmental data and cluster analysis, the environmental conditions of the seven lakes displayed significant differences and they could be classified into three groups: (1) Lake Illawarra; (2) St. Georges Basin and Coila Lake; (3) Durras Lake, Burrill Lake, Conjola Lake, and Swan Lake (Fig. 14.6).

Correlations between environmental factors and phytoplankton assemblages are discussed below to help evaluate the indicative role of phytoplankton as a water quality and eutrophication status indicator for coastal lakes.

14.4.1 The Indicative Role of Phytoplankton Species Composition in Various Habitats

Phytoplankton species composition can be impacted by the physical (e.g., temperature, salinity, pH), chemical (e.g., eutrophication) and even biological conditions. In this study,

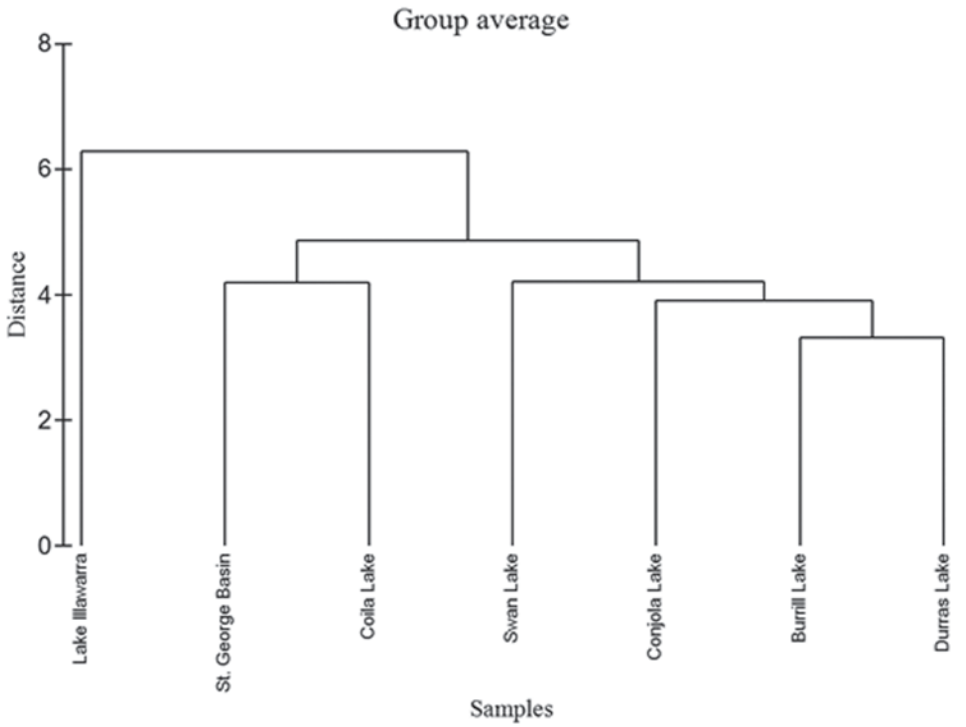

Fig. 14.6 The environmental cluster analysis for seven studied estuaries

the characteristics of phytoplankton species composition well reflected the warm temperate climatic regime in southern NSW, as evidenced by a large number of temperate water species and some warm water species. In addition, these shallow ICOLLs were characterized by extensive estuarine vegetation communities, such as, seagrass, macroalgae, and saltmarsh, and these plants provided suitable habitats and substrata for the epiphytic and periphytic species. As a result, phytoplankton assemblages in these coastal lakes were composed of euplanktonic, tychoplanktonic, epiphytic, and periphytic species (Table 14.3).

Moreover, phytoplankton species composition showed a relationship to the gradient of salinity and pH in the studied lakes. During the sampling period, the proportion of freshwater, brackish, and marine species within the assemblages displayed good consistency with the salinity characteristics of the lakes (Table 14.3; Fig. 14.2): 51% freshwater and brackish species were found in Swan Lake which had the lowest salinity (17.1 psu), 36% in Conjola Lake (salinity: 19 psu), and 26–29% in higher salinity lakes (Coila Lake, Lake Illawarra, St. Georges Basin, Durra Lake, and Burrill Lake).

Mixtures of the seawater (pH close to 8.2) and typical river water (pH = 6–7.5) make estuary pHs generally range from 7.5 to 8.0. During the sampling period, pH values in most estuaries, except for Swan Lake, fluctuated within this normal range and would have had little influence on the phytoplankton species composition. It is difficult to explain why the high pH (mean pH = 8.53) occurred in Swan Lake, but this result is similar to previous studies (Sullivan 2003). Cyanophyta species were usually dominant in alkaline and saline lakes owing to their adaptation to very high pH (10–10.5) (Finlay et al. 1987; Ballot et al. 2005). Increased Cyanophyta species were identified in Swan Lake, and this led to a major difference in Swan Lake phytoplankton communities, compared to all of the other lakes investigated.

Nutrient status was the third factor influencing phytoplankton assemblages. Nutrient-poor conditions not only affect the phytoplankton abundance but also can decrease the species diversity (Dawes 1997). Swan Lake was characterized by very low DIN (average: 0.94 μM) and DIP (average: 0.04 μM) concentrations compared to the other lakes during the sampling period. Only 61 species were identified from this lake, which was much lower than for most of the other lakes (> 100 species).

14.4.2 Role of Phytoplankton Biomass as an Indicator of Water Quality

In this study, Chl a concentrations basically showed a gradient between the seven lakes (Fig. 14.5). Lake Illawarra and St. Georges Basin, characterized by a high degree of catchment urbanization displayed the highest Chl a concentrations, Swan Lake with a small population in the catchment had the lowest nutrient levels and the lowest Chl a concentrations.

Table 14.4 Correlations between Chla and environmental factors in the studied estuaries

Location Items	Lake Illawarra		Burrill Lake		Swan Lake		St. Georges Basin		Conjola Lake		Durras Lake		Coila Lake	
	P	S	P	S	P	S	P	S	P	S	P	S	P	S
DIN	−0.37	0.09	0.26	0.19	0.34	0.11	0.21	0.23	−0.09	0.38	0.10	0.36	−0.52	0.02
DIP	0.20	0.24	−0.03	0.46	0.39	0.08	0.13	0.33	0.03	0.46	−0.41	0.06	0.46	0.04
DSi	−0.04	0.44	0.12	0.34	0.04	0.45	−0.16	0.29	−0.03	0.46	−0.13	0.32	−0.35	0.10
DIN:DIP	−0.31	0.13	0.32	0.14	−0.12	0.34	0.40	0.07	−0.17	0.27	0.09	0.38	−0.41	0.07
DIN:DSi	−0.59	0.01	0.27	0.18	0.05	0.43	0.59	0.01	−0.22	0.21	−0.03	0.46	−0.27	0.16
Temperature	0.58	0.01	−0.03	0.46	−0.72	0.00	−0.49	0.03	−0.02	0.47	0.13	0.33	−0.55	0.02
Salinity	−0.43	0.06	−0.03	0.45	−0.72	0.00	0.07	0.40	−0.02	0.47	0.39	0.08	−0.65	0.00
pH	0.33	0.12	−0.24	0.20	0.02	0.47	−0.11	0.36	−0.18	0.27	0.14	0.31	−0.06	0.41

P pearson correlation, *S* significant (2-tailed)

These results suggest that human activity within the catchment may impact on water quality and therefore the phytoplankton communities. Moreover, some specific information was found in the stepwise multilinear regression between environmental factors and Chl a concentrations (Table 14.4).

In Swan Lake and Coila Lake, the entrances to the sea are closed most of the time and the water areas are small, the variations of temperature and salinity displayed significant impact on Chl a concentrations (Table 14.4).

Phytoplankton biomass has been used as an indicator of nutrient enrichment in many studies and protocols (Fisher et al. 1995; Domingues et al. 2005; Lopes et al. 2007). In this study, low correlations were found between nutrient concentrations and Chl a concentrations for most lakes, except for Lake Illawarra and Coila Lake (Fig. 14.3; Table 14.4). DIN concentrations displayed a significant negative correlation with Chl a in Coila Lake (P: −0.52, S<0.05), indicating P-limitation for phytoplankton growth in this lake; DIN:DSi ratios displayed significant negative correlations with Chl a in Lake Illawarra (P: −0.59, S<0.05), suggesting N-limitation for diatom growth in this lake (Table 14.4). Various hypotheses on nutrient behavior and primary production have been presented for temperate coastal lagoons over the last two decades (e.g., Fisher et al. 1988; Gowen et al. 1992; Froneman 2004). For the majority of coastal lagoons, correlations between nutrients and any single population of primary producers are not often apparent. In estuaries where phytoplankton production is low, overall primary production may be supplemented by benthic algae and/or seagrass. Thus, nutrients are used by many different primary producers and no clear relationship exists with any single producer. Moreover, the impact of unreasonable nutrient ratios on the growth of phytoplankton is as important as nutrient concentration (Dortch and Whitledge 1992). For management, it is important to give a comprehensive assessment of all aquatic vegetation, although phytoplankton can provide important information on ecosystem processes.

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Biogeochemical Indicators of Nutrient Enrichments in Wetlands: The Microbial Response as a Sensitive Indicator of Wetland Eutrophication

15

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Abstract

In wetlands it is still usual to use the same indicators of eutrophication which were developed to study the effects of nutrient enrichment in lakes; however, since hydroecology and biogeochemistry of wetlands is significantly different from lakes, monitoring of these indicators does not allow a good diagnosis of the changes undergone by the wetland ecosystem under nutrient enrichment scenarios. Microbial activities and their respective community responses have been considered as a measure of ecosystem stability and an indicator of ecosystem perturbation through changes on functional properties associated with nutrient cycling. As in most aquatic ecosystems, the addition of a limiting nutrient to wetland ecosystems promotes primary productivity and stimulates microbial processes. As nutrient loading increase, biogeochemical processes in wetlands are altered, changing their concentrations in water and soil, and therefore, nutrient fluxes and cycling. Nutrient enrichment induces changes in soil physicochemical and microbiological characteristics that may then serve as indicators of nutrient enrichment. In this review, a set of microbial community measurements known to be sensitive to nutrient enrichment in aquatic systems, such as extracellular enzyme activities, respiratory activities, microbial biomass C, N, and P, and microbially mediated N and P turnover rates have been used to characterize physiological response of the microbial community to wetland eutrophication. Some indicators as metabolic efficiency and phosphatase activity clearly reflect the main shifts on wetland ecosystem processes induced by nutrient enrichment and may be considered better than those that are currently used to assess the effects of eutrophication. Moreover, the combined use of different ecophysiological measurements such as extracellular enzymatic ratios and microbial biomass under resource allocation models and ecological stoichiometry demonstrates that ecophysiological measures are sensitive indicators of wetland eutrophication. Further studies are needed refining this approach to get the complex biogeochemical variability of the different wetland types, and to move from a site-based heuristic model to a holistic approach, describing eutrophication patterns in wetlands.

Keywords

Eutrophication · Nutrient enrichment · Carbon · Nitrogen · Phosphorus

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15.1 Introduction

Ecosystem evaluation and management consistently requires measures that monitor the present state of a system and characterize its rate of change in response to exogenous disturbances. The biological symptoms of eutrophication in wetlands appear to be similar to those in shallow lakes but the ecosystem biogeochemical responses may be different (Reddy and Delaune 2008; Sánchez-Carrillo and Angeler 2010). The main obstacles for modeling eutrophication in wetlands to find good indicators of ecosystem changes derive from the use of biological communities and water quality standards inherited from the classical studies on eutrophication in temperate lakes. In lakes, phytoplankton biomass increases when the nutrient limiting supply rises (i.e., algal blooms). In shallow lakes, changes are consistent with predictions made by alternative state theory (Scheffer et al. 1993) and the trophic cascade concept (Carpenter and Kitchell 1993): increased nutrient and water turbidity levels, shift the ecosystem from submerged macrophyte dominance to phytoplankton dominance (e.g., Whillans 1996; Chow-Fraser 1998; Álvarez-Cobelas et al. 2001). In wetlands, considering the wide disparity between ecosystem types (e.g., only taking into account hydrogeomorphological aspects; Brinson 1993) and since wetlands are known to function as nutrient transformers in the landscape (Phillips 1996; Gunatilaka 1991; Sánchez-Carrillo and Álvarez-Cobelas 2001) the response of phytoplankton and submerged charophyte communities to nutrient enrichment does not follow a clear pattern.

Nutrient enrichment in wetlands has been shown to influence all trophic levels and its effects include changes in species abundance, replacement, biodiversity loss, and shifts in community structure and composition (Piceno and Lovell 2000; Álvarez-Cobelas et al. 2001; Guntenspergen et al. 2002; Liston et al. 2008). Abiotic shifts induce biotic changes and these, in turn, lead to complex feedback effects on ecosystem metabolism. As nutrient loading increase, biogeochemical processes in wetlands are altered, changing nutrient concentrations in water and soil and, hence, nutrient fluxes among compartments. These ecosystem-wide changes modify conditions within the wetland and alter the physical and chemical environment. The addition of limiting nutrients to wetland ecosystems increases primary productivity and stimulates microbial processes. Organic matter decomposition and nutrient cycling in wetlands depend on the chemical and physical composition of soil, microbial activity and nutrient availability (Wright et al. 2009). Nutrient enrichment has been shown to generate significant alterations for wetland structure and function (Davis et al. 2003) and induce changes in soil physicochemical and microbiological characteristics that may then serve as effective indicators of nutrient enrichment (Corstanje and Reddy 2006).

Microbial communities play a key role in nutrient cycling and organic matter degradation in wetland systems. Wetland soils are relatively rich in functional microbial communities that are capable of utilizing a wide range of electron acceptors, such as O_2, NO_3^-, Fe^{3+}, SO_3^-, and CO_2 (D'Angelo and Reddy 1999; Wright and Reddy 2001a). Environmental and resource conditions form the fundamental forces that control the microbial community size and its dynamics (Corstanje et al. 2007). In wetlands, microbial communities have been shown to respond to nitrogen (N) and phosphorus (P) enrichment, increasing litter decomposition rates (Davis 1991; DeBusk and Reddy 1998). Microbial responses to enhanced nutrient levels are also reflected in changes on indices of microbial activity, such as respiratory activities (White and Reddy 2001) and extracellular activities (Sinsabaugh and Moorhead 1994; Corstanje et al. 2007). Eutrophication in marsh systems has also been associated with increases in microbially mediated C, N, and P turnover rates (Reddy et al. 1999), and increases in soil MB Content as well (Qualls and Richardson 1995). Experimental addition of N and P to natural systems (Newbold et al. 1983) and to enrichment mesocosm experiments (Qualls and Richardson 2000; Newman et al. 2001) have produced significant increases on microbial activity, primarily as a function of their status as limiting factors in the systems under observation. Monitoring the variables associated with the microbial ecophysiology in response to external disturbances, as well as establishing the baseline of the endogenous environment, has provided basic information of changes on ecosystem functioning related with nutrient enrichment (Corstanje et al. 2007). The aim of this chapter is to provide an overview on the use of microbial communities as indicators of wetland ecosystem changes related with eutrophication processes. Since wetlands play a key role on the terrestrial nutrient cycling, this chapter is focused to the effects of nutrient enrichment on both biogeochemical and microbial processes as a reflection of changes in ecosystem functioning. We selected a set of microbial community response measures known to be sensitive to nutrient enrichment in aquatic systems, such as extracellular enzyme activities (Prenger and Reddy 2004), respiratory activities (DeBusk and Reddy 1998; Qualls and Richardson 2000), MBC, N and P, and microbially mediated N and P turnover rates (Reddy et al. 1999). These measures, and their derivatives or simple combinations as well, have been used to characterize individually the microbial community physiological response to changes in its environment (Anderson and Domsch 1990; Sinsabaugh et al. 1997). The focus of this review is to generate an overall assessment of the effectiveness of the microbial community and its ecophysiology as indicators of ecological perturbation generated by nutrient enrichment in wetlands, with a specific emphasis on the microbially mediated organic matter decomposition

and associated nutrient cycling. The final section is devoted to the evaluation of the model of microbial allocation of resources among community indicator enzymes (MARCIE model) as a tool for wetland eutrophication assessment using microbial indicators.

15.2 Summary of the Main Biogeochemical Changes Associated with Nutrient Enrichment in Wetlands

The first step of nutrient enrichment in wetlands is an increasing productivity of wetland plants. High primary productivity associated with nutrient-rich areas has been observed in numerous wetlands (Davis 1991; Childers et al. 2003; Álvarez-Cobelas et al. 2010). It promotes increases of autochthonous organic matter accumulation in wetland soils (Sánchez-Carrillo and Álvarez-Cobelas 2001). Usually, an increase of nutrient loading is linked to hydrological alterations and shifts in vegetation patterns can be expected (i.e., plant species replacement; Green and Galatowitsch 2002; Childers et al. 2003; Álvarez-Cobelas et al. 2008). Therefore, changes in organic matter supply and litter quality can be expected in high nutrient scenarios (Engelhardt and Ritchie 2002). Because microbial activity responds to nutrient loading and hydrology (DeBusk and Reddy 1998; Wright and Reddy 2001), also strong shifts in decomposition rates and nutrient cycling can be expected as wetland become eutrophic.

After prolonged exposure to high nutrient loading an increase of the wetland internal loading can be expected and hence a reduction in nutrient retention occurs. Because sediment suspension into the water column tend to increase the nutrient soluble forms during eutrophication (Reddy et al. 1998), more available nutrients promote more productivity, resulting in a positive feedback process which can last for years. Thus, nutrient loading into these wetlands enhances organic matter decomposition and microbial activity which increases nutrient concentrations in water (Wright et al. 2008). Although decomposition in these wetlands appear to be dominated by anaerobic pathways (denitrification, sulfate reduction, and methanogenesis; Wright and Reddy 2001), aerobic heterotrophic microbial activity is often enhanced by nutrient loading too (Aerts and Toet 1997; Qualls and Richardson 2000). In the Everglades it has been observed that heterotrophic microorganisms are limited by the high C:P ratios of organic matter but external P loading remove this limitation and induce changes in microbial activity (DeBusk and Reddy 1998). However, aerobic CO_2 production could not be related to the content of dissolved nutrients in soils (Wright et al. 2009) but with microbial biomass, which appeared positively related to nutrient loading (D'Angelo and Reddy 1999). While heterotrophic microbial activity is immediately enhanced after the addition of oxygen in nutrient-rich wetland experiments, net soil organic carbon mineralization has not been shown significant differences when other electron acceptors as NO_3^-, SO_4^{2-}, or CO_2 under anaerobic conditions has been used (D'Angelo and Reddy 1999).

Microbial biomass phosphorus (hereafter MBP) in wetland soils responds positively to phosphorus enrichment in wetlands (Qualls and Richarson 2000; Newman et al. 2003). Labile phosphorus (the most available P fraction to vegetation and microbial communities; Ivanoff et al. 1998) has been cited as the most sensitive P fraction to eutrophication in wetland soils and seston (consisted of algae, periphyton and particulate organic matter; White et al. 2006). Microbial biomass C and N (hereafter MBC and MBN) did not consistently respond to nutrient loading (Wright et al. 2008, 2009). MBC and MBN are linked to C and N cycles but cannot be considered sensitive to nutrient loading. Although eutrophication promotes mineralization rates, phosphorous mineralization has been cited as the most responsive microbial indicator to nutrient enrichment in wetlands (Wright et al. 2009).

Increased availability of sulfate in wetlands is known to cause serious eutrophication problems, as S^{2-} produced by SO_4^{2-} reduction interacts with Fe-PO_4^{3-} complexes in the sediment to produce FeS_2 and FeS, resulting in mobilization of phosphate (Smolders and Roelofs 1993; Lamers et al. 1998). High nitrate concentrations in ground waters have been cited to inhibit eutrophication of sulfate-rich freshwater wetlands (Lucassen et al. 2004). Since NO_3^- is an energetically more favorable electron acceptor in anaerobic wetland soils than Fe^{3+} and SO_4^{2-}, high NO_3^- loads function as a redox buffer, preventing the reduction of Fe^{3+} and SO_4^{2-}. Therefore, limited SO_4^{2-} reduction prevents S^{2-}-mediated mobilization of PO_4^{3-} from Fe-PO_4^{3-} complexes. At higher redox potential, reduced Fe^{2+} is oxidized, increasing the content of Fe^{3+} capable to binding PO_4^{3-} (Reddy and DeLaune 2008).

While the typical loading rates of nitrogen and phosphorus in natural and constructed freshwater wetlands exceed proposed critical loads to prevent eutrophication (total phosphorus: 10 kg P ha^{-1} y^{-1}, total nitrogen: 25 kg N ha^{-1} y^{-1}), wetlands continue to have serious problems preserving its structure (species composition) and functioning (nutrient cycling and retention; Verhoeven et al. 2006). The potential impact of climate change on wetlands will promote ecosystem changes because temperature and precipitation are strong determinants of freshwater wetland ecosystem structure and function (Mitsch and Gosselink 2000). Lower water availability will reduce the flushing rate of wetlands as water renewal times increases. It will probably contribute to increase the high nutrient state of wetlands as biogeochemical processes will be promoted. In the same way, because wetlands are a major natural source of greenhouse gases to the atmosphere we may expect changes in the emissions of N_2O and N_2 as a consequence of eutrophication. Nitrous oxide

emissions, which have a global warming potential 310 times that of CO_2 (IPCC 1996), can be enhanced in the future as nitrate availability in wetlands continues to be high owing to increased agriculture pollution. When nitrate availability is high, reduction of nitrate instead of N_2O is energetically favorable for denitrifyers (Barnard et al. 2005). This potential negative consequence of nitrate-rich wetlands is often ignored or downplayed. Thus, there is a great need for additional information about the risk of nitrogen emissions from nitrogen-loaded wetlands (Verhoeven et al. 2006).

15.3 Changes on Carbon, Nitrogen, and Phosphorus Microbial Biomass during Wetland Eutrophication

Most of the biogeochemical transformations are mediated by microbes and are actively involved in regulating transformation and storage of nutrients. Microbial communities respond to vertical gradients caused by the successive depletion of electron acceptors and electron donors conditioned by the oxygen availability. Because of its dynamic nature, microbial biomass (see Box 1 for methods of measurements) has the potential to be a sensitive indicator to detect changes resulting from either anthropogenic impacts or ecosystem disturbance (Reddy and DeLaune 2008). In fact, MBC, MBN, and MBP found in wetlands have been cited to be very sensitive to changes in the substrate nutrient content, according to the nutrient limitation of the microbial communities (Reddy and DeLaune 2008). In nutrient-poor wetlands, P has been reported as the limiting of microbial activity (Amador and Jones 1993; Reddy et al. 1993; Corstanje et al. 2007).

Unlike, MBP, MBC, and MBN may not be sensitive indicators of eutrophication. In a study by Wright et al. (2009) it was reported that MBC and MBN was not responsive to P loading in the Everglades wetland system. Increased response of MBP to P loading in wetlands of oligotrophic Everglades has been reported by Qualls and Richardson (2000).

MBC:MBP ratios have been found to range from 25 (Singh and Singh 1993) to 79–279 in humus-rich soils (He et al. 1997). The MBC:MBP ratio in soils has been suggested to be in the range from 10 to 35 (He et al. 1997). In general terms, all soils reflect higher C:P ratios in P-limited soils (Joergensen et al. 1995a, b; He et al. 1997). Several studies carried out in the Everglades revealed that microbial biomass at oligotrophic wetland soils exhibits significantly higher C: P ratios than that at intermediate and impacted sites (White and Reddy 2000; Corstanje et al. 2007). Significant correlations were observed for MBC and MBN with soil total P ($r=0.50$; 0.70, $p<0.05$) and with total P for the detrital layer ($r=0.65$; 0.41, $p<0.05$), providing evidence that P was likely the limiting nutrient to the microbial biomass in natural Everglades peat soils (Corstanje et al. 2007).

Box 1: Carbon, Nitrogen, and Phosphorus Microbial Biomass by the Chloroform Fumigation Extraction Procedure

Carbon, nitrogen, and phosphorus content of the microbial biomass can be determined by the 24-h chloroform fumigation-extraction (CFE) technique (Brookes et al. 1985; Witt et al. 2000; Truu et al. 2009). Soils are fumigated with chloroform vapor inducing a lysis of microbial cell membranes and, thus, the subsequent release of microbial constituents can be extracted and quantified. While efficient lysis of microbial cells in aerobic soils can easily be achieved with chloroform vapour, Inubushi et al. (1991) proposed the direct addition of chloroform to anaerobic soil in order to overcome limitations in the fumigation efficiency when exposing water-saturated soil to chloroform vapour. First, ethanol-free chloroform needs to be prepared, removing the ethanol from the chloroform by mixing 500 mL over 25 g of basic grade 1 alumina in a flask and stir for 10 min. Triplicate, 15–20 g (wet weight) soil subsamples are taken to carry out the analysis. Fumigations must be done in the fume hood because chloroform is toxic. Samples to be fumigated are placed in 50 mL glass beakers which must be marked with pencil. The beakers with sample soils are put into a vacuum dessicator (if the sample number is high, beakers can be stacked in the dessicator by layering with shelf). A 50-mL beaker or scintillation vial containing ~1 spatula boiling chips and 20 mL of chloroform is placed in the dessicator. Using a vacuum the air inside the dessicator must be evacuated until chloroform boils, This procedure is repeated three more times, venting at the end of each step except at the last time. Then the dessicator (covered with a black garbage bag because darkness prevents the chloroform from breaking down) is left in the dark for 5 days. After this time, the vacuum is released, drawing a vacuum for 1 min and releasing to remove the chloroform (it must be repeated three times); chloroform is then evacuated to the outside.

Sample extraction is done with 30 mL of 0.5 M K_2SO_4 for 30 min on a longitudinal shaker and vacuum filtered through #42 Whatman filter paper. The extract is analyzed for total organic C on a TOC analyzer and subjected to Kjeldahl-N digestion for total nitrogen analysis. MBP is extracted using 25 mL 0.5 M $NaHCO_3$ and is thereafter analyzed by the ascorbic acid colorimetric procedure. MBC is determined by subtracting the extractable total organic C (TOC) in the triplicate controls (nonfumigated) from the triplicate chloroform-treated samples, using an

extraction efficiency (k_{EC}) factor of 0.37. The values of total organic carbon for the nonfumigated (control) samples were defined as extractable or labile C. MBN is determined by subtracting the extractable NH_4-N concentrations of the triplicate nonfumigated samples from triplicate fumigated samples, applying a combined extraction efficiency value (k_{EN}) of 0.54 (Brookes et al. 1985). Finally, the difference in total P between the treated and untreated samples constitutes the MBP, without using any extraction efficiency factor (Ivanoff et al. 1998).

15.4 Microbial Structure and Function as Indicators for Wetland Trophic Status

Although soil microorganisms regulate biogeochemical processes, their distribution and abundance is controlled by environmental and anthropogenic factors. With this premise studies have focused on linking microbial groups with the trophic status of wetlands (Hartman et al. 2008). It is also known that both extrinsic (regional scale including climate change, geographic location) and intrinsic (local scale including nutrient inputs) factors affect in regulating the microbial communities therefore studies that aim to narrow down the specific microbial species as an indicator of trophic status are still very few. Nevertheless, few studies have explained the presence of certain microbial groups at specific sites with varying nutrient content (Castro et al. 2002, 2004; Bowen et al. 2009; Inglett et al. 2011). These studies have defined the potential role of microbial structure (species richness and distribution of the microbial community), and function (metabolic status of microbial groups, carbon utilization patterns) as indicators for the ecological status of the ecosystems including aquatic soils and sediments. Application of techniques such as nucleic acid fingerprinting (denaturing gradient gel electrophoresis, DGGE; terminal restriction length fragment polymorphism, tRFLP; fluorscence in situ hybridization, FISH), lipid biomarkers (phospholipid fatty acid, PLFA; phospholipid ether lipid, PLEL) and community-level physiological profile (CLPP) have been used in several aquatic soil and sediments including freshwater and coastal wetlands (Kowalchuck et al. 1998; Sizova et al. 2003; Castro et al. 2004; Costa et al. 2007; Zhou et al. 2009; Inglett et al. 2011).

A study by Hartman et al. (2008) showed that wetland restoration resulted in a decrease of bacterial diversity, which is an opposite response to that of the terrestrial systems. The bacterial taxa *Acidobacteria* and *Proteobacteria* were reported to be potential indicators of restoration and trophic status. Although specific microbial groups that have been linked to *Acidobacteria* are oligotrophs and they are characterized by slow growth and use of more refractory carbon substrates in their metabolism (Eichorst et al. 2007). Studies with sediments from reservoirs revealed abundance of β *Proteobacteria* in eutrophic regions and γ-*Proteobacteria* in dystrophic regions. The ratio of *Proteobacteria* to *Acidobacter* has been suggested to be a broad indicator of trophic status of terrestrial soils. Whether this could be applied in wetland systems is yet to be seen. In another study by Jackson and Vallaire (2009) in sediments of the Louisiana wetlands with N enrichment a reduction of the microbial diversity and a decreased proportion of α-*Proteobacteria* and *Planctomycetes* were reported.

Studies on specific microbial groups across the phosphorus gradient in the Florida Everglades have shown differences in sulfate reducing bacteria and methanogenic communities. Eutrophic regions have shown the dominance of *Desulfotomaculum* with ability to completely oxidize substrates in the eutrophic areas relative to the oligotrophic region that was dominated with species that incompletely oxidize substrates (Castro et al. 2002). The Florida Everglades are characterized by high number of methanogens that belong to the order of Methanomicrobiales with higher abundance in the nutrient-enriched regions (Castro et al. 2004). Higher abundance of cellulolytic bacteria in P-enriched sites has been reported, being *Clostridium* assemblages in soils significantly correlated with the soil nutrient status. (Uz and Ogram 2006).

Both the shift in the microbial community of periphyton mats from cyanobacteria and large number of epiphytic diatoms to green algae and the declined abundance of epiphytic diatoms have also been noted across a P gradient in the Florida Everglades (McCormick and O'Dell 1996). Within the periphyton mats the shift from cyanobacteria dominated system to a filamentous green algae system has been a common response to phosphorus enrichment in the Everglades (McCormick et al. 1996). Dramatic decreases of cyanobacteria species richness as a result of eutrophication have also been reported by Rejmankova et al. (2004).

Wetland restoration studies also have shown linkages of the microbial community structure and function to biogeochemical parameters including nutrient changes. By comparing phospholipid biomarkers of the overall microbial community in wetland soils, Inglett et al. (2011) have shown increased fungal population and higher ratio of Gram negative to Gram positive bacteria in high sites with OC:N ratio (newly restored sites). Low phosphorus sites (native sites) were characterized with a higher abundance of Gram positive bacteria. Biomarkers for *Actinomycetes* was also found to be positively correlated to the P concentration in soils. Phospholipid fatty acids (PLFA) are present in both eukaryotic and prokaryotic membranes and thereby give a complete

picture of the soil microbial community. PLFA analysis involves the extraction and analysis of phospholipids from microbial cell walls and have been used to measure microbial biodiversity, metabolic status (starved vs. metabolically active cells) and relative abundance of microbial groups (fungi, bacteria, Gram positive, Gram negative, methanotrophs, and sulfate-reducing bacteria; Vestal and White 1989; Zak et al. 1994; Frostegard and Baath 1996). Among the lipid biomarkers, relative increases in abundance of monosaturated fatty acids and decline in branched fatty acids are proposed indicators of high substrate (C) availability in paddy soils (Bossio and Scow 1997). Changes in metabolic status of the soil microbial community and community structure cooccur. Some lipid ratios have been used as sensitive indicators of nutritional stress (Tunlid and White 1992). The accumulation of poly-beta 0 hydroxyalkanoic (PHA) storage compounds relative to PLFA indicates unbalanced prokaryotic growth. In presence of toxicants the ratio of *trans* monoenoic PLFA increases relative to their *cis* homologues. Unfavorable conditions for bacterial growth and the starvation survival mode are indicated by the cyclopropane fatty acids and the ratio of increased saturated to unsaturated fatty acids, respectively (Tunlid and White 1992; Kieft et al. 1994).

Spatial and temporal changes in microbial functional diversity have also been assessed by determining the physiological profiles at community level (CLPP; Garland and Mills 1994). This culture-based approach measures carbon utilization patterns (BIOLOG method) of the heterotrophic microbial communities (Zak et al. 1994). Highly polluted areas in coastal marshes and polluted river sediments have been characterized with high abundance of microorganisms with low functional diversity (Costa et al. 2007; Jacinthe et al. 2010).

15.5 Organic Matter Mineralization and Nutrient Enrichment in Wetlands

Nutrient enrichment has been noted to generally increase organic matter mineralization rates in wetland soils (Davis 1991; Qualls and Richardson 2000), including the mineralization of P. The combination of nutrient availability and changes in the litter source resulted in a shift in litter quality and quantity (Davis 1991; DeBusk and Reddy 1998), with significant increases in carbon- (DeBusk and Reddy 1998), nitrogen- (White and Reddy 2000; Newman et al. 2001) and phosphorus mineralization rates (Newman et al. 2001). The rates of microbially mediated organic matter degradation not only play a pivotal role in nutrient regeneration (Newman et al. 2001), but are also known to respond to numerous environmental perturbations such as eutrophication, modifying ecosystem processes and hence wetland ecosystem structure and functioning.

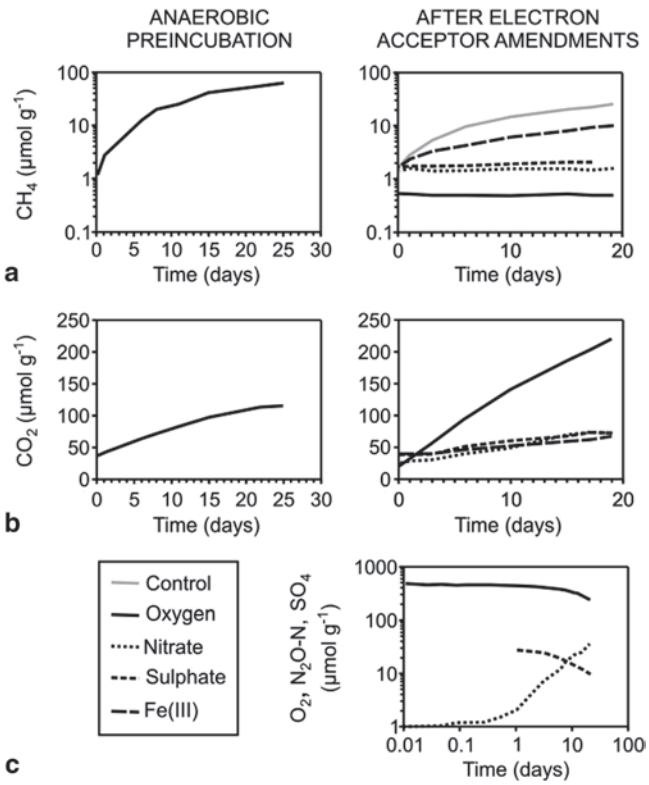

Fig. 15.1 Methane (**a**) and CO_2 (**b**) productions and electron acceptor consumption (**c**) in Alabama Talladega sediment. Anaerobic preincubation denotes time before electron acceptor amendments. (Adapted from D'Angelo and Reddy 1999)

15.5.1 Aerobic and Anaerobic Metabolic Activities in Wetland Soils Exposed to Nutrient Enrichment

A number of investigations have found significant correlations between microbial respiration rates (see Box 2 for incubation methods) in wetland soils and nutrient availability (McKinley and Vestal 1992; Amador and Jones 1993; Aerts and Toet 1997), pH, temperature (Westermann and Ahring 1987; Bridgham and Richardson 1992; Prieme 1994) and electron donors (Burford and Bremner 1975; Yavitt and Lang 1990; Jorgensen and Richter 1992; Crozier et al. 1995; D'Angelo and Reddy 1999; Wright and Reddy 2001). Electron acceptor and donor availability have been found to be dominant in regulating potential rates and modes of organic carbon mineralization in wetland soils (D'Angelo and Reddy 1999). For example, addition of O_2 results in immediate increase in CO_2 emission (Fig. 15.1). Aerobic organic C mineralization rates have been measured to be about three times faster than under anaerobic conditions but there was no significant difference in mineralization rates with NO_3^-, SO_4^{2-}, or CO_2 as electron acceptors (D'Angelo and Reddy 1999). The key of these differences is the bioavailability of organic C in wetland soils: high under aerobic conditions but similar

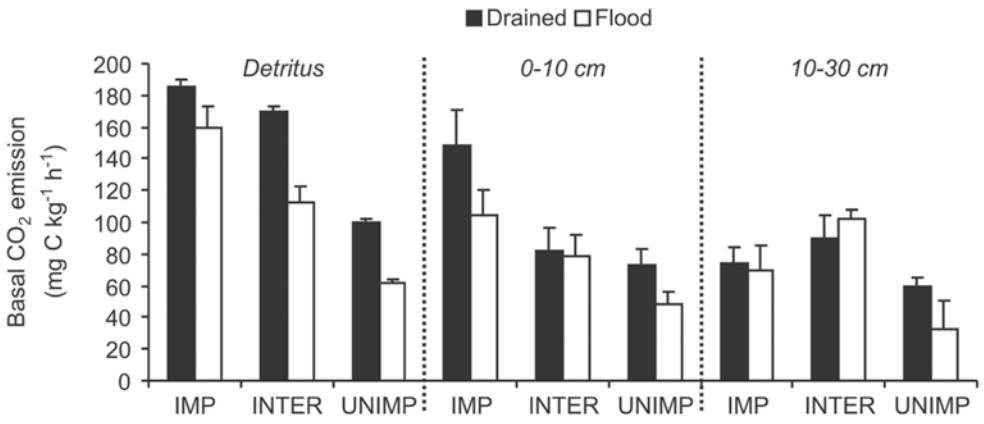

Fig. 15.2 Basal CO_2 emission rates measured in drained and flooded conditions in detritus, at 0–10 cm and 10–30 cm soil depths along the phosphorus gradient in the Wetland Conservation Area WCA-2a at the Everglades. *IMP* impacted, *INTER* intermediate, *UNIMP* unimpacted. Distance from nutrient-rich inflows: IMP: 1.4–3.3 km, INTER: 4.2–7.0 km, UNIMP: 8.4–10.1 km. (Adapted from Wright and Reddy 2001)

under denitrifying, SO_4^{2-} reducing and methanogenic conditions (D'Angelo and Reddy 1999). The sequential reduction of electron acceptors strongly depends on their availability. Higher rates of heterotrophic microbial activities have been measured under sulfate reducing rather than under nitrate conditions associated with higher SO_4^{2-} concentration and lower nitrate concentration which tended to support sulfate reduction and limit denitrification (Wright and Reddy 2001b). Availability of electron acceptors including O_2 and NO_3^- generally result in complete and immediate inhibition of methanogenesis while availability of Fe(III) and SO_4^{2-} often resulted in less effective inhibition (Fig. 15.1; for further information on methane inhibition see D'Angelo and Reddy 1999).

Exposure of soil to O_2, as occurs in periods of low rainfall or low water inputs, increases wetland heterotrophic microbial activity. This increase in microbial activity contributes to enhance organic matter degradation rates and increase regeneration and cycling of nutrients in wetlands which might potentially lead to increased nutrient concentrations in the water column (Wright and Reddy 2001b).

Wright and Reddy (2001) found in northern Florida Everglades high significant heterotrophic microbial activities in wetland soils impacted by P loading, being higher in detritus and surface soils and decreasing with soil depth (Fig. 15.2), according to a lignin content increase in conjunction with decreases in cellulose content (a substrate quality deterioration as measured by the lignocellulose index (LCI), which is the ratio of lignin to cellulose). Additions of substrates containing C, N, and P generally enhanced heterotrophic microbial activity. In field studies, CO_2 production rates in anaerobic soils were approximately 64 % of those observed in aerobic soils (Fig. 15.3; Wright and Reddy 2001). Both CO_2 and CH_4 production rates have been significantly correlated with soil P content and microbial biomass. Sulfate reducing bacteria have been also shown to be enhanced by P loading (Drake et al. 1996); however, besides available P the high SO_4^{2-} concentration in the wetland soil seems to be determinant on sulfate reduction rates (Wright and Reddy 2001). Enhanced heterotrophic microbial activities resulting from P loading has the potential to increase turnover of organic matter which may lead to increase supply of bioavailable nutrients to emergent macrophytes and periphyton and higher nutrient concentrations in the water column (Wright and Reddy 2001).

Box 2: Set Up of Metabolic Activity Incubations

The aerobic metabolic activity assay (see D'Angelo and Reddy 1999; Wright and Reddy 2001b) consisted of 10 g of moist soil placed in Schott media bottles fitted with a NaOH trap, sealed in an atmosphere with 21 % O_2 in order to facilitate aerobic conditions. The anaerobic treatment differed in that the headspace consists entirely of N_2. Soil tubes are then incubated horizontally in the dark at 28 °C during 2 h. The CO_2 in the NaOH trap is released by the injection of HCl through the septum to produce a pH below 2. Headspace CO_2 is measured through gas chromatography equipped with a thermal conductivity detector (temperature at 30 °C) with He as carrier gas and stainless steel Poropak N column (0.3 cm by 2 m) maintained isothermally at 30 °C. In the anaerobic treatments, the headspace CH_4 is analyzed by means of gas chromatography equipped with a flame ionization detection (detector temperature at 110 °C) with N_2 as carrier gas and a stainless steel Carboxen 1000 column (0.3 cm by 2 m) maintained isothermally at 160 °C.

Differences in net heterotrophic respiration can be assessed over short time periods (hours) with simple substrates because the rate limiting steps of soil organic matter decomposition have been removed by providing a readily hydrolizable substrate. For substrate-induced respiration (SIR) measurements, soil samples are supplemented with glucose at an excess concentration of 25 mg C g $soil^{-1}$ and then proceed as in the previous cases.

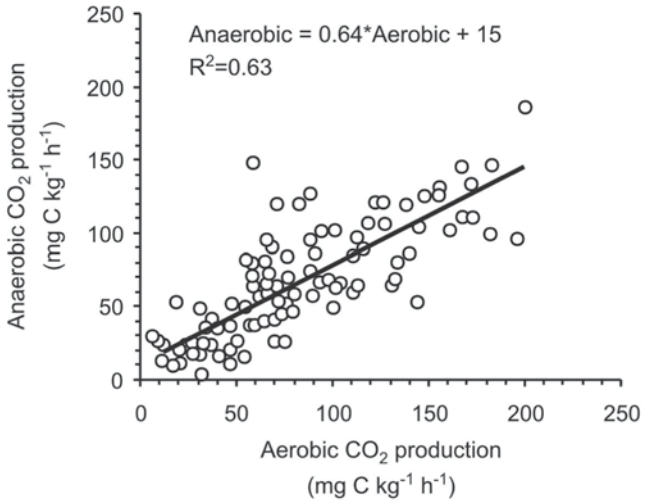

Fig. 15.3 Relationship between basal and substrate induced CO_2 production rates under drained conditions (aerobic) and under flooded conditions (anaerobic) measured in soils in the Wetland Conservation Area WCA-2a at the Everglades. Data from wet and dry seasons were considered. (Redrawn from Wright and Reddy 2001)

15.5.2 Mineralization of Nitrogen and Phosphorus during Wetland Eutrophication

Measurements of potential mineralization of N and P (PMN and PMP; see Box 3) using wetland soil samples have been used successfully to assess the effects of nutrient enrichment on the nitrogen and phosphorus cycling. Higher rates of organic matter mineralization occur in the detrital layer, decreasing with soil depth. In the Everglades at the Water Conservation Area 2a, White and Reddy (2000) and Corstanje et al. (2007) found rates of PMP significantly higher in the nutrient impacted areas compared to the unimpacted sites. PMN has also been negatively correlated with distance from nutrient-rich inflows (White and Reddy 2000). Overall, PMN rates have been significantly correlated with several soil properties including MBC ($r=0.81$) and N ($r=0.85$), total P ($r=0.65$) and extractable NH_4^+ ($r=0.78$) with significant negative correlations with total N ($r=-0.48$). The organic-rich wetland soils have a low redox potential and may contain a thin (2–4 mm) oxidized layer owing to high available C coupled with high microbial activity (Wright and Reddy 2001b). The low O_2 status of the flooded soil can result in the near complete inhibition of the autolithotrophic conversion of NH_4^+ to NO_3^-. Therefore, the concentration of extractable NH_4^+ provides a good indication of *in situ* N mineralization rates in flooded soils (Ross et al. 1995). The strong relationship observed between PMN rate and the size of the microbial pool (MBC and MBN) is likely one of causation (White and Reddy 2000). Mineralization is a microbial-mediated process and given a substrate with a similar C:N ratio, one could expect differences in total active microbial biomass to influence the rate at which inorganic N is liberated from the organic fraction. In addition, total P has been significantly correlated with PMN rate indicating an increase in inorganic N release from soil with increasing total P. This result suggests that in wetlands availability of P to the microbial pool controls the organic N mineralization as observed in other organic and inorganic soils (White and Reddy 2000). The effect of continual P loading over longer terms (many months to years), not only resulted in increased microbial activity but also an increased size of the microbial pool. It seems that inorganic P concentrations had a direct influence on increasing the specific heterotrophic microbial activity responsible for net N mineralization of native soil organic matter.

PMP and PMN can also be expressed as a function of total P and N by means of cumulative potential P, N turnover rates (PMP/total P and PMN/total N expressed in mg mineralized P or N g^{-1} total P or total N) and as a function of MBP and MBN (PMP-, PMN-quotients as PMP/MBP and PMN/MBN, respectively, expressed in d^{-1}). Both expressions take the advantage of normalizing the mineralization rates according to the available nutrients and the size of the microbial loop (Corstanje et al. 2007). The cumulative potential P turnover rates and the PMP-quotient result significantly higher in wetland soils receiving nutrient enrichment (Corstanje et al. 2007). High cumulative P turnover rate indicates that a larger pool of P is being mobilized in excess of the increase in soil P content. Inversely, the microbial communities in nutrient-rich sites are relatively inefficient with the P obtained from organic matter mineralization as PMP-quotient levels appears to be significantly high. The combination of PMP-quotient, and cumulative P turnover rates in nutrient impacted wetlands describes a very efficient microbial community that initially responded to the increases in P availability by rising biomass (P immobilization) and extending P mineralization to pools previously unattainable (Corstanje et al. 2007). Corstanje and Reddy (2006) highlight that a general increase in the P turnover rates can be observed as a result of the P loading while there appeared no effect of the nutrient loading on the metabolic coefficient (qCO_2, the proportion of aerobic basal respiration (CO_2 production) to MBC; Anderson and Domsch 1990; see Sect. 15.6; Fig. 15.4). The nutrient loading as such did not seem to generate stress as to affect the microbial C metabolism, but did increase P metabolism.

PMN-quotient and the cumulative potential N turnover pool did not demonstrate significant differences in enriched soils of Everglades compared to sites having no impact (Corstanje et al. 2007). The aforementioned variability in the levels of PMN associated with the soil total P probably reflects increases in microbial biomass as a result of the alleviation of P-limitation. An increase of the cumulative potential N turnover along with the soil nutrient content reflects higher MBN and higher N-acquiring enzyme activities, probably contemporaneous to the overall increase in microbial biomass as a result the alleviation of P-limitation.

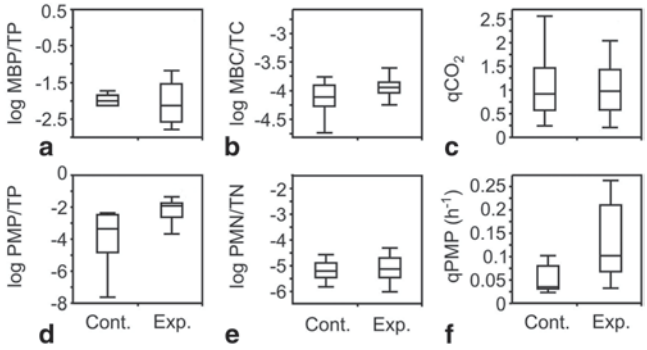

Fig. 15.4 Box and whisker plots of the relative proportion of microbial biomass in the overall P and N pools (**a**, **b**), the metabolic quotient (qCO_2; **c**), the proportion of P and N turnover (PMP and PMN) as fractions of the total P and N pools (**d**, **e**) and the P turnover (PMP) per mesocosm biomass (**f**) in the surface soils (from detritus to 5 cm depth). Data from the experiment by Corstanje and Reddy (2006) at the mesocosm scale using raceways containing organic peat soil planted with *Cladium* sp. and *Typha* sp. communities. *Cont* control, *Exp* experimental

Box 3: Incubations for Assays of Potential Mineralization

Potential mineralizable nitrogen and phosphorus (PMN and PMP) are measured using 10-day anaerobic incubations respectively. Equivalent of 10 g (PMN) or 0.5 g (PMP) dry weight soil samples are placed in 50 mL serum bottles and mixed with 5 mL of distilled deionized water. Bottles are capped with butyl rubber stoppers and sealed with aluminum crimps. The headspace is evacuated and replaced with 99.99 % O_2-free N_2 gas. The samples are subsequently incubated in the dark at 40 °C for 10 days, after which, 30 mL of 0.5 M K_2SO_4 (PMN) or 20 mL of 1.0 M HCl (PMP) are injected into the serum bottle and after shaken for 1–3 h on a longitudinal shaker and centrifuged for 10 min at 4,000 g. The supernatant is extracted and filtered (0.45 μm) and the filtrate stored at 4 °C until analysis. A second set of samples of equivalent weights (controls of PMN and PMP reported as starting total N and P) is directly extracted with 35 mL of 0.5 M K_2SO_4 (PMN) and 25 mL of 1.0 M HCl (PMP) as described previously. PMN extractions are finally analyzed for NH_4-N through total Kjeldahl nitrogen procedure. HCl extract for PMP is analyzed by the ascorbic acid. The difference in K_2SO_4 and HCl–extractable N and P over the 10-day incubation period constitutes PMN (mg N kg^{-1} d^{-1}) and PMP (mg N kg^{-1} d^{-1}).

Substrate-induced N mineralization can be assessed over short time periods (h) by adding simple substrates as amino acids. The basic setup for this assay is similar to the PMN procedure, including replicates for aerobic (drained sample) and anaerobic (flooded sample) incubations: to 10 g of dry weight soil samples placed in 50 mL serum bottles 1.0 ml of solution containing 400 mg L-*alanine* ($C_3H_7NO_2$)-N L^{-1} is added; then the samples are mixed to distribute the spike solution and soil aggregates must be broken using a glass rod to maximize the soil volume in contact with air (aerobic samples). Drained sample bottles are capped incubated in the dark for 4 h at ambient temperature (~28–31 °C). Flooded sample bottles are capped, purged with O_2-free (99.99 % pure) N_2 gas for 5 min, and then incubated in the dark for 4 h at ambient temperature. At the end of the incubation all samples are extracted with 50 ml of 2 M KCl: bottles are agitated on a longitudinal shaker for 1 h and vacuum filtered through #42 Whatman filter paper. The supernatant is collected and stored at 4 °C until subsequent automated colorimetric analysis for NH_4-N. These incubations can also be performed under field conditions by submerging the bottles in the water at the site of interest.

15.6 Extracellular Enzyme Activities and Nutrient Availability in Soil Wetlands

In most aquatic ecosystems, a significant portion of energy and nutrient flow is through the microbial loop, a mechanism by which detrital carbon and nutrients are recycled into the foodweb (Sinsabaugh and Foreman 2003). Organic matter in wetlands is composed of high molecular weight polymeric compounds, of which only a small portion is readily available to microbial communities (Chróst 1991). These complex organic compounds must be first hydrolyzed into low molecular weight compounds which can be directly transferred to cells, oxidized and used as an energy source through the activity of extracellular enzymes secreted by microbes (bacteria and fungi) and plant roots (Chróst 1991; Sinsabaugh et al. 1991). From the biogeochemical point of view, the importance of extracellular enzymes lies in that they catalyze the rate limiting steps of decomposition and nutrient cycling (Sinsabaugh 1994). Extracellular enzymes (see Box 4 for measurement methods) are generally defined as enzymes that have crossed the cytoplasmic membranes of the microbial cell. Most of the extracellular enzymes are bound to the solid surface but a small fraction remains in the soil pore water. The latter exoenzymes contained in soil pore water are most susceptible to microbial degradation and chemical alteration. Surface-bound enzymes may not be as effective as free enzymes because of a slow rate of substrate

diffusion to the sites where enzymes are present (Reddy and DeLaune 2008). The synthesis of enzymes is regulated by the presence or absence of the readily available substrates. Presumably, the production of enzymes is relatively expensive at the cellular level, resulting in a hydrolytic activity that reflects the relative need of the microbial communities (Sinsabaugh et al. 1997). If production of extracellular enzymes is maximized in terms of resource allocation by the microbial communities, the relative activity of N and P-acquiring enzymes relative to the permanent C requirement is an indication of the levels of N or P limitation that these microbial communities experience in that particular environment (Sinsabaugh and Moorhead 1994).

Several enzymes are known to be involved in the cycling of nutrients and can be used as potential indicators of nutrient cycling processes in wetlands. Glucosidase catalyzes the hydrolysis of glycosides, resulting in the release of a β-linked monosaccharide (Eivazi and Tabatabai 1990). Phenol oxidase mediates the breakdown of lignin-containing compounds and depends on oxygen availability (McLatchey and Reddy 1998). Cellulose and lignin-degrading enzyme activities have been correlated with degradation rates of detritus (Sinsabaugh 1994; McLatchey and Reddy 1998). Phosphatase activity plays an important role in the regeneration of inorganic P through its catalysis of the breakdown of organic P esters to inorganic P (Chróst 1991). Phosphatase is often repressed by high dissolved reactive P concentrations in a process referred to as feedback inhibition (Chróst 1991; Wright and Reddy 2001). Protease enzymes are important in the wetland N cycle and function in the breakdown of proteins, resulting in the release of NH_4-N (Ladd and Butler 1972). Arylsulfatase enzymes catalyze the hydrolysis of sulfate esters resulting in the release of SO_4^{2-}, being important to S cycling processes in wetland soils (Tabatabai and Bremner 1970). Finally, dehydrogenase enzyme activity is used as a measurement of the overall biological activity in soils (Trevors et al. 1982).

While decomposition rates have been strongly correlated with the activity of lignocellulose degrading enzymes (Sinsabaugh et al. 1992), the enzymes involved in the other macronutrient (N, P, S) cycles are now receiving increasing attention. The activity of these extracellular enzymes is affected to some degree by the nutrient loading because bioavailable nutrients can potentially decrease their activity (Newman and Reddy 1993). Therefore, measurements of extracellular enzyme activities can be useful as an early warning indicator of the impacts of nutrient enrichment in wetlands (Newman et al. 2003). Phosphatase enzymes are known to be release by microorganisms in response to a decrease in the internal P pool; therefore it is possible to expect their inhibition in response to P enrichment (Jansson et al. 1988). Inverse relationships between soil total P and alkaline phosphatase activity have been found in wetlands (Cotner and Wetzel 1991; Newman and Reddy 1993; McLatchey and Reddy 1998; Wright and Reddy 2001; Newman et al. 2003; Corstanje and Reddy 2006; Hill et al. 2006; Corstanje et al. 2007) as well in other aquatic systems (Cotner and Wetzel 1991; Nausch and Nausch 2000; Shackle et al. 2000). The nutrient enrichment mesocosm-scale study performed by Corstanje and Reddy (2006) during 18 months using organic peat soil planted with *Cladium* sp. and *Typha* sp. clearly drawn the temporal effects of the nutrient loading in the soil phosphatase activity (Fig. 15.5): nutrient loading resulted in a significant decrease of the extracellular enzyme acid phosphatase activity across both plant communities, in contrast to β-glucosidase activity, which varied primarily along with the plant community. Unfortunately, these relationships between phosphatase activity and soil P content may be also attributed to other factors: for example, phosphatase production is assumed to be regulated by the microbial internal P pool, which may not accurately reflect the P pool outside of microbial cells (Chróst 1991). Inorganic P additions also have been reported to have stimulatory, inhibitory, and no effect on phosphatase activity (Wright and Reddy 2001; Sánchez-Carrillo, unpublished data). Phosphatase activity can vary depending on the carbon availability although this relationship does not appear to be clear enough: in fact an increase of activity by the availability of labile carbon in the soil (Wright and Reddy 2001), a decrease of activity with the increase of sediment total carbon

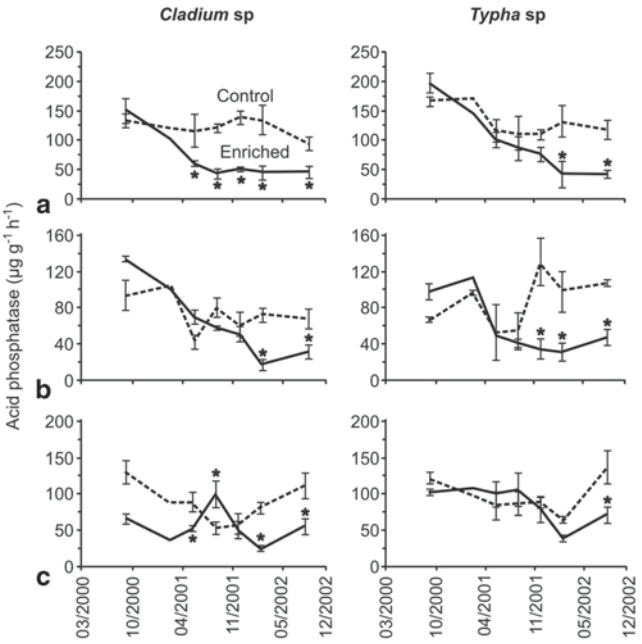

Fig. 15.5 Time course of extracellular acid phosphatase activities measured in two vegetation communities during a mesocosm experiment developed to test the effects of nutrient enrichments. **a** Detritus, **b** 0–5 cm of soil depth, **c** 5–10 cm of soil depth. The *asterisk* indicates significant differences ($p<0.05$) between treatments. (Redrawn from Corstanje and Reddy 2006)

concentration (Hill et al. 2006) and even no effect related to carbon availability (Shackle et al. 2000) have been reported. When readily metabolized soluble carbon is freely available, it has been suggested that there is no need for microorganisms to acquire it enzymically (Chróst and Rai 1993). Further work is needed to assess the role of carbon quality controlling not only glucosidase activity but also both peptidase and esterase enzyme activities under different nutrient limitation scenarios in wetlands. Other variables such as soil porewater P according to pH and aerobic/anaerobic conditions determine the phosphatase activities (e.g., the acid phosphatase activity becomes higher in aerobic soils whereas the alkaline phosphatase activity appears to be higher in anaerobic soils; McLatchey and Reddy 1998). Since extracellular enzyme activities did not depend on a single environmental variable (e.g., Kang et al. 2005), other multivariate approaches need to be considered in order to refine the potential of phosphatase activity as a sensitive indicator of nutrient dynamics in wetlands.

The relationships between organic N and extracellular enzyme activities appear to be more diffuse than those of P because N is associated with nucleic acids, polysaccharides, proteins, and humic complexes. Unlike extracellular phosphatases which typically have wide substrate preferences, each of these N pools is accessed by discrete enzyme systems. In aquatic systems, the relationship of protease and aminopeptidase activities to protein degradation has received the most attention (e.g., Mayer 1989; Billen 1991). Aminopeptidase activity has been shown to be induced by low N conditions and noncompetitively inhibited by inorganic N (Chróst 1991; Boschker and Cappenberg 1998; Montuelle and Volat 1998; Ainsworth and Goulder 2000; Nausch and Nausch 2000). Protease activities have also been studied in soils (e.g., Ladd 1972) but rarely in the context of their relationship to N acquisition by microorganisms in relation with N supply. Protease enzymes are considered as the main responsible for the supply of bioavailable N in the substrate (Paul and Clark 1996) and, therefore, as the exoenzyme addressing and controlling the nitrogen cycle in wetlands (Wright and Reddy 2001; Schimel and Bennett 2004). Protease activity demonstrated a significant positive relationship with gross organic nitrogen mineralization, with greater protease activity under aerobic conditions than under anaerobic conditions (McLatchey and Reddy 1998). Protease activity appears to be inversely correlated with soil NH_4^+ concentration: at high substrate concentrations for microbial growth, some hydrolysis products such as NH_4^+ cannot be assimilated by microorganims and are released into the soil solution; thus an excess of NH_4^+ may repress some enzyme activities (Wright and Reddy 2001).

McLatchey and Reddy (1998) developed a comprehensive list of the empirical relationships of the main variables regulating microbial processes in wetlands (Table 15.1).

Table 15.1 Empirical relationships of the main variables regulating microbial processes in wetlands. C_m, N_m, and P_m are mineralization rates (mg kg^{-1} d^{-1}); MBC, MBN, MBP are MBC, N, and P (mg kg^{-1}); SIR_{Gluc} and SIR_{Acet} are the substrate-induced respiration with glucose and acetate respectively (mg Ckg^{-1} d^{-1}); β-Glucosidase and phosphatase activities are expressed as mg *p*-nitrophenol Ckg^{-1} h^{-1}, and protease activity is expressed as mg tyrosine Ckg^{-1} h^{-1}. (From McLatchey and Reddy 1998)

$C_m = 0.03*MBC + 47$	$R^2 = 0.93$
$N_m = 0.36*MBN - 35$	$R^2 = 0.53$
$P_m = 0.72*MBP - 31$	$R^2 = 0.77$
$SIR_{Gluc} = 0.19*MBC + 76$	$R^2 = 0.93$
$SIR_{Acet} = 0.09*MBC + 106$	$R^2 = 0.81$
$C_m = 5.2*(\beta\text{-Glucosidase}) + 6.7$	$R^2 = 0.91$
$N_m = 7.5*(\text{Protease}) + 8.6$	$R^2 = 0.78$
$P_m = 0.3*(\text{Phosphatase}) - 4.5$	$R^2 = 0.72$

Significant relationships were found between carbon, nitrogen, and phosphorus mineralization and their respective microbial biomass. Similar relationships were asserted for wetland soils amended with either glucose or acetate. Statistical analyses also have shown strong correlations between β-glucosidase activity and C mineralization, between protease activity and N mineralization and between phosphatase activity and P mineralization (Table 15.1).

Considering P loading as a major cause of wetland eutrophication, the responses of extracellular enzyme activities are quite different. In P-limited wetlands, where there have been most of studies, alkaline phosphatase activity was the only enzyme affected by P loading. Other enzymes, such as arylsulfatase, β-glucosidase, protease, and phenol oxidase, were not affected by P loading. The measures that are most closely associated with the P cycle (alkaline phosphatase activity, potential mineralizable P, and MBP) were those that responded to the nutrient enrichment within a relatively short time scale (6 months; Corstanje and Reddy 2006). However, like all ecological processes, extracellular enzyme activity is regulated by a suite of environmental variables that interact over a wide range of scales (Sinsabaugh 1994): at the ecosystem level, enzyme production is a function of microbial activity which is regulated by moisture, temperature, and nutrient availability; at the microenvironmental level, temperature and moisture continue to influence the activity of released enzymes, but responses are modulated by enzyme-substrate interactions such as inhibition, adsorption, stabilization, and humification. The combination of all these processes and scales often results in a nonlinear response of the extracellular enzyme activity to the limiting nutrient. Owing to the complex nature of organic matter, degradation requires the concerted activity of multiple classes of enzymes. In fact, while the activity of enzymes involved in C acquisition, i.e., lignocellulase activity, can be linked to litter characteristics and decomposition rates, the activity of enzymes involved in N and P acquisition appears to be more closely tied to the

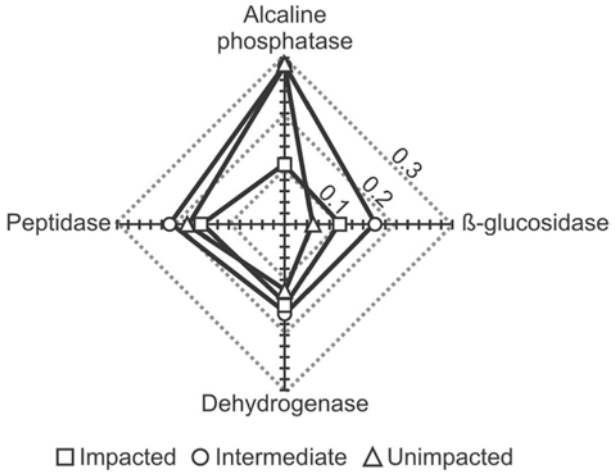

Fig. 15.6 Radar graph of the relative mean extracellular enzyme activities (detritus and 0–10 cm soil; normalized relative to their respective maximal activities) according to the nutrient-enrichment impact at three sites in the Water Conservation Area 2a of the Everglades. (Adapted from Corstanje et al. 2007)

environmental availability of these nutrients. The combined relative activity of the enzymes has been proposed by Sinsabaugh et al. (1997) as a model for microbial response to environmental conditions. Enzyme activities are normalized through a simple index model which incorporates all the enzyme data into one pool without the bias associated with the different ranges of activity. The enzyme data are standardized to a 0–1 scale by dividing the activity recorded for a specific enzyme by the maximum value obtained for that enzyme during the study. Average enzyme activity for each sampling date is calculated by summing the relative activities of each enzyme and dividing the total by the number of enzymes assayed. This mean activity is then integrated over time to obtain estimates of cumulative activity per day. Corstanje et al. (2007) used this approach to assess the relative mean enzyme activities at different levels of nutrient enrichment in the Everglades (Fig. 15.6). They found that alkaline phosphatase activity was a significant response variable when describing the P dynamics in this system, protease and dehydrogenase activities showed little response and β-glucosidase activity was higher in the intermediate impacted site.

An analysis of the combination of enzymatic activities has also been assayed using a meta-analysis (Corstanje et al. 2007), in which the independent variables (enzymatic activities) are combined to generate a single test. This analysis allows a comparison of the overall enzymatic activities considering both the site characteristics and the possible enzymatic offsets. For example, in the cited study, the meta-analysis results demonstrated the existence of a threshold type (step) response in soil microbial activity as compared to the more progressive change in the soil nutrient characteristics. It implies that microbial indicators such as extracellular enzymatic activities function effectively as early warning signals of disturbance.

Using ecological stoichiometry theory, extracellular enzymatic ratios have recently been used to assess the energy and nutrient dynamics in different ecosystems including wetlands. The stoichiometric theory extends the elemental composition of cellular components to ecological processes and organization using cellular growth models and ratios of nutrient availability. These theories are connected through the threshold element ratio (TER, elemental C:N or C:P ratio at which control of metabolism switches from energy supply –C– to nutrient supply –N, P–) and the growth rate theory. Because ecoenzymatic activity reflects microbial metabolism and environmental resource availability, Sinsabaugh et al. (2009) proposed that ratios of commonly measured ecoenzymatic activities are related to threshold element ratio and microbial growth rates. Using ecoenzymatic activities C:N:P ratios of soil and sediments from lotic, lentic, and soil systems it was found that heterotrophic microbial communities of diverse composition shared a common pattern of functional organization. The mean C:N:P stoichiometry of these enzyme activities indicates that the rates of supply of assimilable substrates from the respective C, N, and P reservoirs are on average similar in magnitude, and thus that proximate limitations on microbial production may readily shift between C, N, and P (Sinsabaugh et al. 2009).

Extracellular enzymatic activities have also been used as sensitive indicators of nutrient dynamics in wetland ecosystems at broad scales. Hill et al. (2006, 2010) linked microbial enzyme activities to regional-scale anthropogenic stressors in the coastal wetlands of the Laurentian Great Lakes and in the Upper Mississippi, Missouri and Ohio rivers. Extracellular enzyme activities were correlated with wetland sediment and water chemistry and stoichiometry, atmospheric N deposition, the agricultural stress gradient and the hydrological turnover time. Using canonical correlation analysis a strong correlation between extracellular enzyme activities and the percent of the catchment in anthropogenically dominated land uses, including agriculture and urban development, was revealed. Microbial enzyme regulation of carbon and nutrient dynamics may be sensitive indicators of anthropogenic nutrient and carbon loading.

Box 4: Assays for the Measurements of Extracellular Enzyme Activities

Soil samples for enzyme activity assays must be previously 2 mm sieved and duplicate controls (without substrate) and samples must be done in order to evaluate sample variance.

1. *Dehydrogenase activity* (global metabolic activity of the microbial community; Enzyme Commision Number (EC) 1.1.1.1): using the substrate 2-p-iodophenyl-3-p-nitrophenyl 5-phenyl tetrazolium cloride (INT) as electron acceptor it occurs the reduction of tetrazolium salts and the appearance of formazan (Skujins 1976; Garcia et al. 1993): add 0.4 mL of distilled water and 0.2 mL of INT (0.4% mass/volume) to 1 g of soil sample and incubate for 20 h in darkness at 20 °C. Then add 10 mL of methanol and stir vigorously during 1 min, then filter. Controls are prepared adding 0.6 mL of distilled water. Read spectrophotometrically the absorbance of the extract at 490 nm against a calibration curve prepared with INTF (iodonitrophenyl formazan) at different concentrations. The results are expressed as mg INTF g^{-1}.
2. *β-glucosidase activity* (C-acquiring enzyme –degradation of cellulose; EC 3.2.2.21): using the artificial substrate p-nitrophenyl-β-D-glucopyranoside (PNG) and measuring spectrophometrically the released p-nitrophenol (Tabatabai 1994): add 2 mL of 0.1 M maleate buffer (pH = 6.5) and 0.5 mL of PNG (0.05 M) to 0.5 g of soil sample. Incubate and shake in a water bath at 30 °C for 1.5 h. Chill at 2 °C for 15 min. Then add 0.5 mL of 0.5 M calcium chloride and 2 mL of 0.5 M sodium hydroxide. Centrifuge for 15 min at 2,000 g. Dilute if appropiate and spectrophotometrically read at 398 nm. Controls must be prepared by adding the substrate just after incubation and prior to cooling tubes. The standard curve is performed with p-nitrophenol (PNP). The results are expressed in µmol PNP g^{-1} h^{-1}.
3. *Phenol oxidase* (EC 1.10.3.2) and *peroxidase* (EC 1.11.1.7) (C-acquiring enzyme–oxidation of lignin an other poliphenol) *activities*: using L-3,4-dihydroxyphenylalanine (DOPA) as the substrate and measuring spectrophotometrically at 450 nm. For phenol oxidase, add 50 µL of 25 mM of DOPA to soil samples. For peroxidase assays add 50 µL of 25 mM DOPA plus 10 µL of 0.3% H_2O_2. Negative control samples for phenol oxidase must be prepared containing 200 µL of acetate buffer and 50 µL of DOPA solution; blank samples must contain 200 µL of sample suspension and 50 µL of acetate buffer. For peroxidase, negative control and blank samples also must contain 10 µL of H_2O_2. Microplates are incubated in the dark at 20 °C, approximately 4 h for peroxidase and 18 h for phenol oxidase. Finally, activity is quantified by measuring absorbance at 450 nm using a microplate spectrophotometer. The results are expressed in nmol h^{-1} g^{-1}.
4. *Protease activity* (N-acquiring enzyme): using sodium caseinate as substrate and measuring spectrophotometrically the released tyrosine, using the Folin-Ciocalteu reagent (Ladd and Butler 1972): add 2.5 mL of 50 mM Tris buffer solution (pH 8.1) and 2.5 mL of sodium caseinate (2%) to 0.5 g of soil sample. Incubate and shake in a water bath at 50 °C for 2 h. Cool at 2 °C for 20 min to stop the reaction. Add 2.5 mL of trichloroacetic acid (15%) and later centrifuge at 8,000 g for 10 min. Subsequently 2.5 mL of supernatant are taken and added to tubes with 3.75 mL of an alkaline reagent solution, which are incubated for 15 min at ambient temperature. After this time add 2.5 mL of Folin-Ciocalteu reagent (33%) and finally centrifuge at 2,000 g for 10 min. Dilute if appropriate, and read in the spectrophotometer at 700 nm. The results are expressed in mg tyrosine g^{-1} h^{-1}.
5. *Leucine aminopeptidase activity* (N-acquiring enzyme; EC 3.4.11.1): using L-Leucine p-Nitroanilide (LPN) as substrate the hydrolysis of the peptide bond of leucinamide is measured spectrophotometrically at 410 nm (Mitz and Schlueter 1958): add 2 mL of 50 mM Tris buffer solution (pH 8) and 2 mL of LPN (2 mM) to 0.5 g of soil sample in a 5 mL polypropylene tube. Cap tubes, place them in zip lock bags, put bags in the platelet mixer and incubate for 2 h at 20 °C. Spin the reaction suspensions for 2–3 min in table top centrifuge and pipette 2 mL of supernatant into a 15 mL test tube. Add 0.2 mL of 1.0 N NaOH to each test tube to terminate the reaction and develop the color. Add 8 mL of distilled water to each test tube and vortex. Finally, read absorbance of each tube at 410 nm. Zero the spectrophotometer with distilled water. The results are expressed in µmoles LPN g^{-1} h^{-1}.
6. *Alkaline phosphatase activity* (P-acquiring enzyme; EC 3.1.3.1): using as substrate p-nitrophenyl phosphate (PNPP) and measuring spectrophometrically at 398 nm the absorbance of released p-nitrophenol gives a yellow coloration (Tabatabai 1994): Add 2 mL of 0.1 M maleate buffer (pH 6.5) and 0.5 mL of PNPP (0.115 M) to 0.5 g of soil sample. Incubate and shake in a water bath at 30 °C for an hour and a half. Cool at 2 °C for 20 min to stop the reaction. Add 0.5 mL of 0.5 M calcium chloride and 2 mL of 0.5 M sodium hydroxide and centrifuge at 2,000 g for 10 min. Read spectrophotometrically the absorbance at 398 nm. Controls are prepared adding substrate just after the incubation and prior to cooling tubes. The results are expressed in µmoles PNPP g^{-1} h^{-1}.

A faster alternative but of course also more expensive to aforementioned colorimetric methods for enzyme activities are the fluorimetric assays. The basic setup for fluorescence assays is described by Marx et al. (2001) and Pritsch et al. (2004) and microplates for the subsequent use of microplate readers must be used. The microplate assay allows a large number of soil samples and/or enzymes to be analysed in a short time. The substrates used are conjugates of the highly fluorescent compounds 4-methylumbelliferone (MUB) and 7-amino-4-methyl coumarin (AMC). The main advantage of using fluorimetrically labelled substrates is that product formation can be measured directly in the microplate without previous extraction and purification of the product.

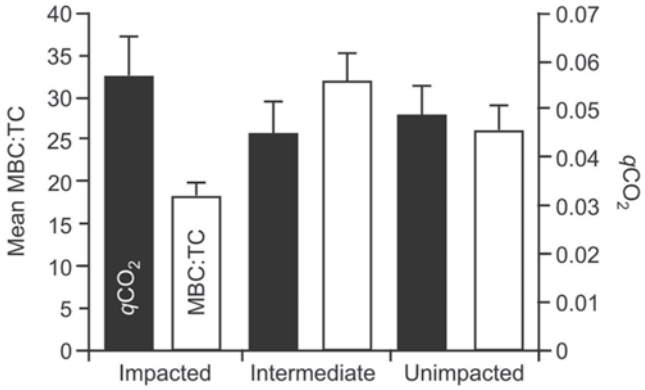

Fig. 15.7 Soil microbial biomass to total carbon content ratios (MBC:TC) and the soil microbial metabolic quotient (qCO_2) in relation with the nutrient enrichment impact at three sites in the Water Conservation Area 2a of the Everglades. Data from detritus and 0–10 cm soil. (Adapted from Corstanje et al. 2007)

15.7 Organic Matter Quality Changes and Effects on Microbial Responses

Significant changes in wetland plant community composition affect the litter quality and hence the microbial community response (Corstanje and Reddy 2006). Presence or absence of plants and plant species richness influence nutrient retention and enzyme activities in constructed wetlands (Zhang et al. 2010). Litter quality has been significantly correlated with the microbial response measures. Factors such as the lignocellulose composition (DeBusk and Reddy 1998) and the nutrient content of the plant litter material (Kögel-Knaber 2002) all determine the response of the microbial communities in concert with a direct response to enhanced levels of nutrients. However, there are still no studies jointly evaluating effects of eutrophication, changes in litter quality and effects on microbial transformations. Although the above mentioned lignocelluse index (LCI) can be used as an qualitative indicator of the organic matter quality, the proportion of aerobic basal respiration (CO_2 production) to MBC, i.e., metabolic coefficient qCO_2 (Anderson and Domsch 1990) can be considered as a better sensitive response variable to soil organic matter quality (Kaiser and Heinemeyer 1993; Corstanje and Reddy 2006). The suggestion is that large qCO_2 coefficients are an indication of disturbed ecosystems (Dilly et al. 1997), in which microbial communities respire more per unit biomass than in stable systems. The loss in the nutrient cycling efficiency (i.e., perturbation) then appears when increased concentrations of microbial biomass result in a decrease of the microbial metabolic activity to microbial biomass ratio (Wardle 1993). Similarly, PMP and PMN, which are assumed to be primarily microbially mediated (Bridgham et al. 1998), reflects potential P and N-turnover rates at a given site and is a function of the biodegradability of the litter organic P and N (see Sect. 4.2).

Using qCO_2 coefficients and the MBC to total C ratio, Corstanje et al. (2007) measured the changes on metabolic efficiency in the Everglades associated with the nutrient enrichment (Fig. 15.7). While no significant changes in the levels of qCO_2 were found among impacted and unimpacted sites, the increases in primary productivity, C deposition and MBC associated with the nutrient influx at the impacted sites did not change the metabolic efficiency as compared to the P-limited unimpacted sites. This microbial response possibly reflects the imposition of the system to a new limitation on microbial heterotrophic activity associated with the substrate quality. This could imply that, after the disturbance caused by the nutrient enrichment, wetlands become relatively open systems which are less efficient on nutrient cycling.

15.8 The Optimal Resource Allocation Model MARCIE as an Indicator of Microbial Community Responses Under Wetland Eutrophication

Like all ecological processes, the biotic responses to eutrophication are subject to a complex hierarchy of regulatory constraints. At the ecosystem level, the increase in productivity reflects the local dynamics of macronutrient supply and community structure, neither of which can be assessed easily. At the cellular or population level, the increase on productivity can be described in terms of the kinetics of substrate utilization (Sinsabaug et al. 1997). Considering the biogeochemical character of wetlands as nutrient transformers dominated by the microbial pool activity, this latter scale of changes should be the most appropriate to measure the effects of eutrophication on ecosystem biogeochemistry stability. Needs and demands of microbial communities change as nutrient availability is altered. This is the key to assess the fingerprint of microbial community responses under wetland

eutrophication. An optimal resource allocation model can then be very useful to assess the effects of wetland nutrient enrichment on the microbial communities through enzyme activities comparing with reference (unenriched) wetland sites.

The microbial allocation of resources among community indicator enzymes (MARCIE) model was originally developed by Sinsabaugh and Moorhead (1994) and subsequently evaluated (Sinsabaugh and Findlay 1995; Sinsabaugh et al. 1997; Sinsabaugh et al. 2002). It describes the enzymatic activity of microbial communities in relation to microbial production through a first order model that includes specific C, N and P allocation factors. It is based on the premise that (i) ectoenzymatic hydrolysis of complex molecules is the rate-limiting step in microbial activity; (ii) that ectoenzyme synthesis is controlled at the level of transcription by induction and repression-derepression mechanisms that are linked to environmental nutrient availabilities (Chróst 1991) and (iii) that to community level these regulatory processes appear as an optimal resource allocation strategy (Sinsabaugh et al. 1997). In this model, extracellular enzymes are grouped into three main categories: those involved in carbon acquisition (E_C), those involved in nitrogen acquisition (E_N), and those involved in phosphorus acquisition (E_P). Enzyme activities serve as indicators of the relative availability of C, N, and P. Because of their common regulatory action, it is assumed that the activities of the many enzymes in each group are sufficiently correlated such that the activity of one, or preferably a few, enzymes in each group can act as an indicator for the whole group. The basic form of this model for microbial production is:

$$P = k_C E_C$$

where P is the production rate and k_C is a first-order rate constant (production per unit E_C activity). The expression of C-acquiring enzymes is constrained by the need to enzymatically acquire N and P; thus E_C can also be expressed as a fraction of total extracellular enzyme production ($E_T = \Sigma(E_C, E_N, E_P)$) whose value is dependent on N and P availability:

$$P = k_C E_T/(1 + E_N/E_C + E_P/E_C)$$

The model can be evaluated by the fact that (i) the microbial production rates are proportional to total enzyme activity E_T, and (ii) the microbial productivity is a function of specific nutrient acquiring enzymes $E_T/(1+E_N/E_C+E_P/E_C)$, therefore exhibiting specific resource allocation versus generic resource allocation. Two ratios of interest can then be formulated: E_C/E_N and E_C/E_P or the ratios between the amounts of enzyme activity associated with C acquisition to the enzymes involved in N and P acquisition. In addition these ratios become indices of relative N and P limitation. Pearson's correlation coefficients between E_T and $E_T/(1+E_N/E_C+E_P/E_C)$ can be used to assess the preferential resource allocation: a strong positive coefficient approaching 1 indicates no difference in resource allocation (i.e., relative quantities of enzyme production), whilst weak to no significant correlations indicate the prevalence of one or more enzymes (Corstanje et al. 2007). Log plots of E_C/E_N vs E_C/E_P are used to assess the relative P availability (E_C/E_P) versus the relative N availability (E_C/E_N) (Fig. 15.8).

Since the lumping of cellulases with polyphenol oxidative enzymes in an E_C term is problematic because both enzyme classes are differentially regulated in relation to N, Sinsabaugh et al. (2002) recommend separate E_C into two terms, one for enzymes involved in the breakdown of holocellulose, E_{Cel}, and one for enzymes involved in the oxidation of lignin and other polyphenols, E_{ox}.

Microbial responses may vary based on litter quality (lignin to cellulose content), the type of electron acceptors present (oxidases vs. hydrolases) and the actual microbial community composition (fungal phytases vs. bacterial and plant phosphatases). Thus, the ideal situation is to include in the assessment more than one enzyme representative of the C, N, and P cycles each. E terms are calculated on a relative basis because of the different scalar ranges of the assays and because assay methodology varies widely. The activity of each enzyme is standardized to a 0–1 scale by dividing each value by the maximum value for that enzyme in the data set. For an E term that includes multiple enzymes activities, the standardized values of each constituent enzyme are averaged. Usually E_P included the standardized activity of acid or alkaline phosphatase; E_N the mean standardized activity of proteases, aminopeptidases or glucosaminidases; E_C the mean standardized activity of β-glucosidase, cellobiohydrolase, endoglucanase, phenol oxidase, or peroxidase (E_{cel} includes the mean standardized activity of β-glucosidase, cellobiohidrolase, endoglucanase while E_{ox} considers the standardized activity of phenol oxidase or peroxidase).

Significant higher levels of E_C/E_P and E_C/E_N ratios have been found at wetland nutrient-enriched sites compared with reference (pristine) areas (Fig. 15.8; Table 15.2; Corstanje et al. 2007; Penton and Newman 2007). Greater E_C/E_P values reflect a decrease in apparent P control on C mineralization as a consequence of lower C:P ratios derived from P influx. Higher E_C/E_N at nutrient-enriched sites has been cited owing to elevated β-glucosidase associated with microbial production (Penton and Newman 2007). The protein content of the organic matter source modifies the E_C/E_N ratio; the higher protein percentage of algae compared with macrophyte tends to decrease the E_C/E_N values (Penton and Newman 2007).

This approach helped clarify how nutrient enrichments induce shifts on microbial allocation of resources. In the Everglades, in terms of enzyme activity the nutrient impacted

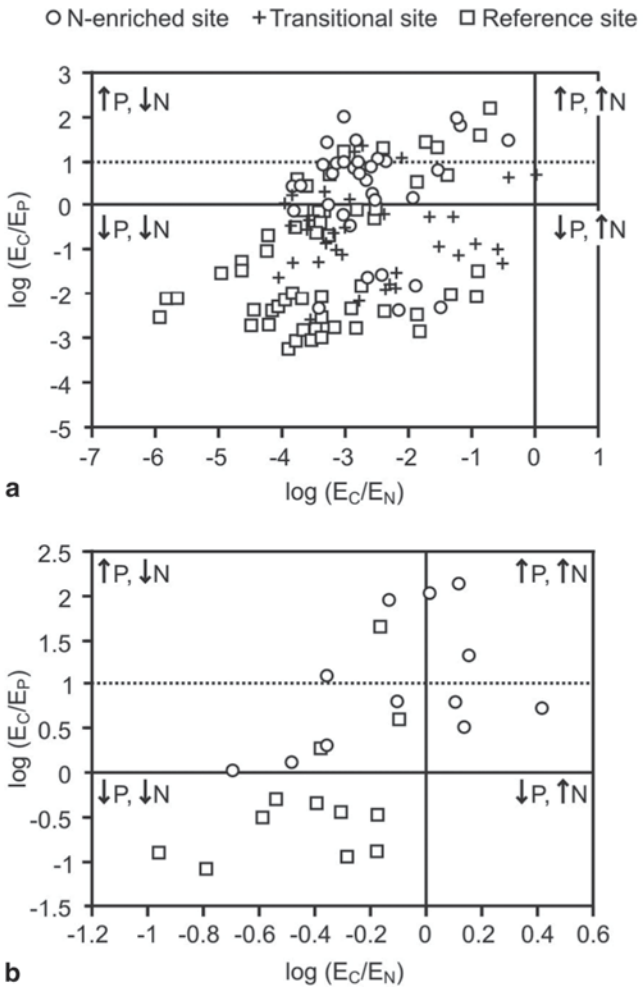

Fig. 15.8 Log plot of the ratios of exoenzymes involved in carbon, nitrogen and phosphorus acquisition (E_C/E_NvsE_C/E_P) showing the microbial resource allocation according to the MARCIE model for nutrient enriched and reference (unenriched) sites of the Everglades. *Vertical arrows* indicate the relative availability of N and P for the microbial consortia. **a** Comparison among enriched, transitional, and unimpacted sites at the Water Conservation Area 2a (Corstanje et al. 2007); **b** Comparison between nutrient enriched and referenceconditionsin four distinct hydrologic units of the Everglades: the Loxahatchee National Wildlife Refuge (LNWR), Water Conservation Area 2a (WCA-2a), Water Conservation Area 3a (WCA-3a), and Taylor Slough (Penton and Newman 2007)

areas promote the prevalence of generalist microbial communities (i.e., no difference in resource allocation) while reference sites increased specialist communities (Table 15.2; Corstanje et al. 2007). Large shifts in N and P dynamics have also been observed between enriched and reference sites by Penton and Newman (2007) using E_C/E_P and E_C/E_N ratios (Fig. 15.9). Both studies suggest the existence of an environmental threshold on total P concentration below which changes in enzyme-based resource allocation will not occur. Concurrently with E_C/E_P and E_C/E_N, in this latter study the E_C/E_{OX} values were examined to assess the effects of nutrient enrichment on lignin degradation. Small increases in E_C/E_{OX} values were measured in nutrient-enriched sites which might indicate an apparent reduction of lignin control on C mineralization. The repression of phenol oxidase activity could be attributed to either the greater N availability (higher E_C/E_N values) coming from exogenous sources and the lower oxygen availability in the nutrient-enriched areas.

Table 15.2 Microbial resource allocation according to the MARCIE model for nutrient enriched (ENR), intermediate (INT), and reference (no enriched, REF) sites in the Water Conservation Area 2a of the Everglades.Different letters denote significant differences. (1) The correlation between E_T and $E_T/(1+E_N/E_C+E_P/E_C)$ evaluates the microbial trade-off in enzyme production: a strong positive correlation coefficient indicates no preferential resource allocation; the bolded correlation coefficient are significant. (From Corstanje et al. 2007)

	ENR	INT	REF
E_C/E_N	1.00*a*	1.75*a*	0.88*b*
E_C/E_P	2.06*a*	0.86*b*	0.74*c*
$E_T=E_C+E_N+E_P$	0.37*a*	0.59*b*	0.52*b*
$E_T/(1+E_N/E_C+E_P/E_C)$	0.10*a*	0.12*a*	0.05*b*
Pearson correlation coefficient[a]	*0.69*	*0.53*	−0.15

[a] Correlationbetween E_T and $E_T/(1+E_N/E_C+E_P/E_C)$

15.9 Conclusions

Considering the biogeochemical character of wetlands as nutrient transformers dominated by the microbial pool activity, this latter scale of changes should be the most appropriate to measure the effects of eutrophication on ecosystem biogeochemistry stability. Needs and demands of microbial communities change as nutrient availability is altered. This is the key to assess the fingerprint of microbial community responses under wetland eutrophication. The concept of utilizing microbial ecophysiological measures as indicators of wetland disturbance is particularly reinforced by the shift on microbial resource allocation associated with nutrient enrichment. Soil nutrient content changes gradually as a result of the influx of nutrients while soil microbial measures such as enzyme activity exhibited a threshold response. These distinct, abrupt changes in microbial community activity as compared to the more progressive change in the soil chemical characteristics indicate that microbial indicators function effectively as early warning signals of wetland eutrophication (Corstanje et al. 2007).

Eutrophication in wetlands promotes significant changes in wetland plant community composition which affect the litter quality. Microbial responses in turn vary based on litter quality, the type of electron acceptors present and the microbial community composition. The first symptom of nutrient enrichment in wetlands is an increase of the microbial biomass resulting in a loss in the nutrient cycling (metabolic) efficiency because microbial metabolic activity to microbial

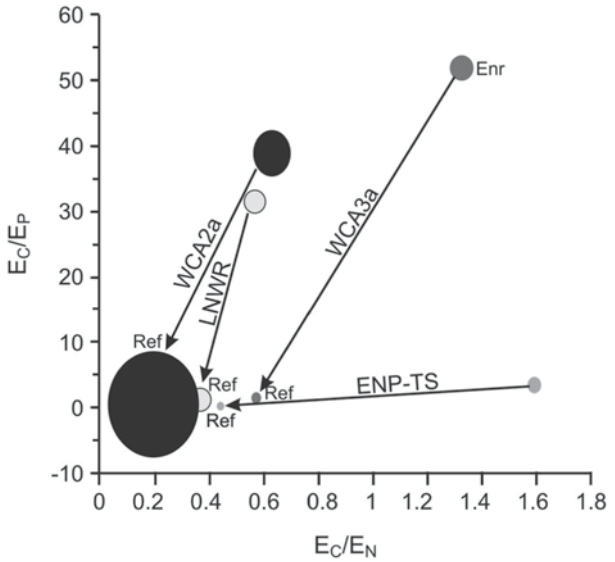

Fig. 15.9 Relationship between the ratios of exoenzymes involved in carbon, nitrogen and phosphorus acquisition (E_C/E_N and E_C/E_P)with the exoenzymes involved in the oxidation of lignin and other polyphenols to total carbon extracellular enzymes (E_C/E_{OX}; represented by the numerically identified bubble size) in four distinct hydrologic units of the Everglades:the Loxahatchee National Wildlife Refuge (LNWR), Water Conservation Area 2a (WCA-2a), Water Conservation Area 3a (WCA-3a) and TaylorSlough (ENP-TS). The *arrows* indicate shifts from the enriched (*Enr*) to the corresponding reference (*Ref*) sites in each area. (Redrawn from Penton and Newman 2007)

biomass ratio decreases. This metabolic effect can be easily measured by the proportion of aerobic basal respiration (CO_2 production) to MBC (qCO_2 coefficient) and the MBC to total C ratio.

Although phosphatase activity is usually repressed in response to P enrichment, contrary effects have also been reported because extracellular enzyme activities did not depend on a single environmental variable. Extracellular enzyme activity is regulated by a suite of environmental variables that interact over a wide range of scales (at ecosystem and microenvironmental levels). Owing to the complex nature of organic matter, degradation requires the concerted activity of multiple classes of enzymes. The combined relative activity of the enzymes reflects more clearly the microbial response to environmental conditions. Extracellular enzymatic ratios, resource allocation models and ecological stoichiometry have properly assessed the energy and nutrient dynamics in wetlands and proved to be the best available tools for use as sensitive indicators of eutrophication. However, further studies are needed refining this approach to get the complex biogeochemical variability of the different wetland types, and to move from a site-based heuristic model to a holistic approach, describing eutrophication patterns in wetlands. A composite analysis in which biotic and abiotic measurements are analyzed collectively and a more quantitative direct comparison of the microbial ability of individual measures to distinguish impacted and reference sites, might strengthen the microbial ecophysiological measurements as key indicators of wetland ecosystem perturbation.

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Task of Mineral Nutrients in Eutrophication

16

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Abstract

Eutrophication refers to natural or artificial addition of nutrients to water bodies and its effects on the aquatic life. When the effects are undesirable, eutrophication may be considered a form of pollution. Excessive nutrient loading to lakes and rivers causes eutrophication that has negative impacts on the biota together with rendering the water body unusable for human beings. Expensive cleaning operations have to be undertaken if the water has to be used for any domestic or industrial purpose. In fact improvement in the water quality of many freshwater and most coastal marine ecosystems requires reductions in both nitrogen and phosphorus inputs. Based on nutrient status and productivity, an aquatic system can be classified into the following three types: (1) Oligotrophic: water with poor nutrient status and productivity; (2) Mesotrophic: water with moderate nutrient status and productivity; (3) Eutrophic: water with rich nutrient status and high productivity. Massive amount of mineral nutrients and organic matter are added in water reservoirs in the form of sewage effluents, organic wastes, agricultural runoffs, excreta, and exudates of living beings. These contain plenty of phosphates coming in large quantities owing to the use of soaps, detergents, and water softeners. In some eutrophic water bodies, dense population of planktonic algae develops. The phenomenon is called water or algal blooms because of the fast growth rate of algal population. The presence of mineral nutrients in concentrations sufficient to support the huge population of planktonic algae is the prerequisite for the formation of algal blooms. All activities in the entire drainage area of a lake or reservoir are reflected directly or indirectly in the water quality of these water bodies. In many lakes and reservoirs, wastewater is the main source of nutrients since untreated wastewater or wastewater treated only by conventional methods usually contains nitrogen and phosphorus. The loading of N and P to the world's rivers, lakes, and oceans is very strongly influenced by human population densities, the population densities of livestock, and land use environmental implications of N and P to the biosphere. Phosphorus removal from wastewater is an effective approach for prevention of eutrophication in closed water systems. The role of potassium in microorganisms responsible for biological phosphorus removal in waste water is more important. Further studies are needed to examine how the inorganic

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formation of calcium carbonate can control the fate of nutrients in water bodies added by anthropogenic activities. Magnesium is essential for chlorophyll synthesis and, thus, acts as a limiting factor for the growth of phytoplankton. Therefore, depletion of magnesium reduces the phytoplankton population. As an essential element, therefore, Mg often limits the growth of primary producers such as algae, other aquatic plants, cyanobacteria, and photosynthetic bacteria. The regulation effects of iron should be considered besides nitrogen and phosphorus during the treatment of eutrophication of lakes. Studies of algal spectral properties under different iron supply would be meaningful for determining the bloom and developing the remote sensing warning system of lake eutrophication. The present review covers the definition and concept and types of eutrophication, adverse effects of eutrophication on quality and functioning of aquatic ecosystems, causes and consequences of eutrophication, and the task of mineral nutrients in the process of eutrophication.

Keywords

Algal bloom · Eutrophication · Nitrogen · Nutrient loading · Phosphorus · Potassium

16.1 Introduction

Eutrophication is the process by which a water body acquires a high concentration of nutrients, especially phosphates and nitrates. These nutrients promote excessive growth of algae. As the algae die, a huge amount of organic matter is acted upon by decomposing organisms that deplete the available oxygen of water, causing suffocation and the death of aquatic fauna and flora. In the middle of the twentieth century, eutrophication was recognized as a problem for the first time. Since then, the biologists have been studying it extensively in order to prevent further eutrophication of vital bodies of water around the world (Khan and Ansari 2005; Yang et al. 2008; Ansari et al. 2011). Although it is a natural slow-aging process, many human activities have led to widespread eutrophication in rivers, streams, lakes, and oceans around the world. When eutrophication is accelerated, it becomes a severe problem, adversely affecting the quality of water and the diverse organisms living therein. Eutrophication, caused by human activities, is known as "nutrient pollution." Mineral nutrients runoff from the agricultural farms is a leading cause of eutrophication worldwide. Furthermore, surface runoffs, dust and organic debris, excreta and exudates of animals also raise the nutrient content in the water bodies. The decomposition of biodegradable pollutants releases hazardous elements which often threaten the biodiversity in the water body. The eutrophication-accelerated plant and animal biomass that develops in the water body often becomes a nuisance. As the nutrients enter the water supply, they result in an outburst of plant growth in water, specifically that of algae, known as algal bloom. Eutrophication-affected lakes and rivers often turn bright green or red according to the type of algae forming the algal bloom. Algal blooms severely reduce the available oxygen in the water and, hence, ultimately lead to loss of animal species in these water bodies owing to suffocation. For instance, there is a gigantic dead zone, which lacks animal life in the Gulf of Mexico because of eutrophication. For several decades, the attempts have been made to prevent eutrophication of water bodies around the world (Ansari et al. 2011).

16.1.1 Types of Aquatic Systems

Based on nutrient status and productivity, aquatic systems can be classified into the following three types:

a. *Oligotrophic system*: a water body with poor nutrient status and productivity
b. *Mesotrophic system*: a water body with intermediary or moderate nutrient status and productivity
c. *Eutrophic system*: a water body with high nutrient status and productivity

These three systems demarcate a biomass gradient that ranges from nutrient-poor to nutrient-rich water bodies, supporting low (oligotrophic), medium (mesotrophic), and high (eutrophic) biomass habitats. Nixon (1995) explained the process of eutrophication in terms of increase in the rate of supply of organic matter to the ecosystem. This definition has gained worldwide acceptance and may be the most frequently used quantitative measure of eutrophication. In estuaries, organic matter occurs in the form of particulate organic matter (POM), e.g., plant debris, detritus, phytoplankton, and as dissolved organic matter (DOM), e.g., humics, mucopolysaccharides, peptides, and lipids. The distinction between POM and DOM depends on the methods used to separate the two fractions (e.g., filtration, ultrafiltration, centrifugation, dialysis). In addition, the rate of supply of different forms of organic matter is highly variable in natural ecosystems and is significantly affected by the factors such as land use characteristics of the watershed (rural, agricultural, urban), hydrology, and climatology. (Paerl 1997; Guo et al. 1999). Allochthonous organic matter (AOM) is transported into the estuary primarily from watershed runoff and river inflow (usually the primary source) or from coastal waters through tidal inlets (secondary source). AOM is generated within the system, mostly through photosynthesis by primary produc-

ers or by benthic regeneration of organic matter. In estuary habitats, the dominant primary producers are phytoplankton, benthic microalgae, epiphytes, sea grasses, and other submerged aquatic vegetation. Primary productivity, in many estuaries, is measured by either $^{14}CO_2$ uptake or O_2 evolution, determining the photosynthetic rate. Rates of photosynthesis and estimates of primary production of an estuary provide databases for assessing long-term trends in trophic state. According to Nixon (1995), the trophic status of an estuary can be classified as oligotrophic (< 100 g C m^{-2} y^{-1}), mesotrophic (100–300 g C m^{-2} y^{-1}), eutrophic (300–500 g C m^{-2} y^{-1}), or hypertrophic (> 500 g C m^{-2} y^{-1}).

16.1.2 Accelerated Eutrophication

Natural eutrophication takes place very slowly. But, human activities have accelerated the process of eutrophication in the past several decades. Huge amount of mineral nutrients and organic matter are added in water reservoirs in the form of sewage effluents, organic wastes, agricultural-field runoffs, excreta, and exudates of living beings. These effluents contain plenty of phosphates, which are used in large quantities in soaps, detergents, and as water softeners. The aquatic bodies acquire more nutrients from these effluents in a day than it would do in a year under undisturbed natural conditions. Runoff from agricultural fields carries huge amount of nitrates and phosphates applied as fertilizers, which promote luxuriant growth of algae and other aquatic plants in the water bodies (Khan and Ansari 2005; Ansari et al. 2011). Following the eutrophication, bacteria and blue green algae fix atmospheric nitrogen, while the phosphates present in rocks and detritus at the bottom are solubilized by microbial activity. Later, a rich microbial and animal population also develops. Ultimately, silt and organic debris collects in the bottom and the water body turns into a shallow and muddy pond, then to a marsh and finally to a dry land. Thus, the water body which could have served us as a reservoir of fresh water, fishes, and other products for hundreds of years becomes useless within a span of a few years only (Khan and Ansari 2005; Ansari et al. 2011; Dokulil and Teubner 2011).

16.1.3 Algal Blooms or Water Blooms

In some eutrophic water bodies, dense population of planktonic algae develops, turning the water green within a short span of time. The phenomenon is called as formation of algal blooms or water bloom because of the fast growth rate of algal population. Such waters are useless for human beings as it is very difficult and costly to remove the microscopic green plants. The entire mass of planktonic algae may often die suddenly. It results in large quantities of dead and decaying organic matter, changing the taste and odor of water unfavorably. So far, the scientists have not been able to solve the problem of water blooms successfully. Nonetheless, the problem arises as a consequence of rapid nutrient enrichment of water body or accelerated eutrophication. Apart from nutrient enrichment of water bodies, water blooms arise because of some other factors also. Water blooms are usually found associated with certain specific conditions such as:

- Water bodies where there is very little diversity in aquatic species. Factually, algal blooms are usually composed of only one or two species.
- High organic matter content of the water is usually associated with water blooms. This usually turns the pH on the alkaline side.
- Little amount of nitrates or phosphates in the water body is also associated with formation of algal blooms because most of the nutrients remain lodged inside the algal cells. In support, a high concentration of these nutrients has been recorded prior to the formation of blooms (Landsberg 2000; Sellner et al. 2003; Ansari et al. 2011).
- Hot and humid climate and high light intensity usually results in the development of algal blooms.

Presence of high concentrations of mineral nutrients to support the huge population of planktonic algae is the primary requirement for the development of algal blooms. Addition of nutrients to aquatic bodies show that even if enough nitrogen and phosphorus is provided to an aquatic system, bloom formation fails to occur because almost all the added nutrients are quickly absorbed by aquatic biota, specifically the Algae, which accumulate large quantities of nitrogen and phosphorus in their cells in order to support their multiplication for future cell generations (Landsberg 2000; Sellner et al. 2003).

Apart from high levels of dissolved organic material in water in which bloom formation occurs, a number of algae are known to produce organic secretions (Landsberg 2000; Anderson et al. 2002; Sellner et al. 2003). The usual abundance of only one or two species in a water bloom may also be ascribed to the inhibitory action of extracellular products, which suppress the growth of other aquatic forms. Water blooms are usually developed in hot and humid condition with high light intensity. These climatic conditions promote intense microbial activity, which result in quick decomposition of organic matter leading to abundant quantity of dissolved organic matter in the water body. Dissolved organic matter, thus produced, releases plenty of nutrients for algal growth. In tropical and subtropical regions, hot and humid conditions also results in thermal stratification in aquatic vegetation. With the sun heat, upper layers of water turn hot, and being lighter these layers stay above the cooler layers present beneath them. In the upper layers, oxygen is dissolved from the atmosphere; while, intense sunlight supports active photosynthesis leading to luxuriant algal growth.

Humidity and the absence of air circulation prevent active evaporation, which prevents cooling of upper water layers. During formation of algal bloom, nutrient limitation is

possibly avoided owing to already present plenty of nutrients in the algal cells accumulated earlier. Besides, intense microbial activity also releases a number of nutrients in a water body rich in organic matter. Hence, dense populations of algae appear in the upper layers. As the day advances, upper water layers become saturated with oxygen as a result of algal photosynthesis. The presence of large population of planktons in upper water layers prevents light to go to deeper areas. Lower layers, thus, suffer from oxygen deficit that stimulates anaerobic activity of the aquatic organisms. The anaerobic systems may produce a number of organic substances, which are intermediate metabolites of the algal metabolism, thus further facilitating the luxuriant growth of algae. In the evening as sunlight weakens, upper water layers get cooled. Thus, oxygen-saturated water, having algal planktons, sinks down leading to mixing of water layers at deeper areas. The added oxygen increases the microbial activity at deeper areas resulting into mineralization of the organic matter that was partially decomposed during the day. Thus, plenty of nutrients are present in the lower layers, which are partly derived from the bottom mud and rocks and partly from decomposition of organic matter. Algal cells rapidly take up and accumulate these nutrients. Experimental evidences suggests that a number of organic substances released by microbial systems are intermediate products of plant metabolism, which are taken up by algal cells as such and incorporated in their metabolism (Landsberg 2000; Sellner et al. 2003). As sun comes up the following day intense light promotes active photosynthesis and planktons rise to the upper layers, which get again warmed up. The whole process is repeated day by day and, thus, the algal bloom acquires a permanent nature (Landsberg 2000; Sellner et al. 2003).

Eutrophication progresses following the six stages:

ADDITION OF MINERAL NUTRIENTS
(Specifically nitrates and phosphates)
↓
LUXURIANT GROWTH OF ALGAE
↓
SUDDEN DEATH OF ALGAE
(Due to certain factors)
↓
FLOURISHING GROWTH OF BACTERIA
(O_2 consumption)
↓
LACK OF OXYGEN
↓
SUFFOCATION
(Death of aquatic organisms)

16.2 Nutrient Loading During Eutrophication

Nitrogen and phosphorus are two major nutrients responsible for eutrophication. Nitrogen has a more complex pathway than phosphorus. Nitrogen can enter and leave the water body in the form of free nitrogen gas through atmospheric exchange. Carbon has been shown to diffuse into the water column at rates sufficient to meet the needs of photosynthesizing cells (Molot and Dillon 1997). Phosphorus, on the other hand, may enter the water body through the inflows, precipitation, and dry fallout and from sediments; it may be removed by sedimentation and through the outflow. The different pathways of nitrogen, phosphorus, and carbon cycles make phosphorus the obvious choice for eutrophication control in the lake. A certain reduction of phosphorus input will generally result in a greater reduction in algal biomass compared with the same reduction of nitrogen. Furthermore, the reduction of nitrogen input without a proportional reduction in phosphorus creates low N/P ratio, which favors nitrogen-fixing nuisance algae, without any reduction in algal biomass (Babin et al. 1989). Hence, phosphorus content is considered the key variable for eutrophication control in a lake. Total phosphorus content includes crystalline, occluded, absorbed, particulate organic, soluble organic, and soluble inorganic phosphorus. In terms of decreasing availability, there are three biologically available phosphorus fractions of phosphorus, viz. soluble reactive phosphorus (a mixture of dissolved inorganic and organic phosphorus), soluble unreactive phosphorus (It includes dissolved phosphorus fed by persulfate oxidation, which is available for phytoplanktons by enzymatic hydralization that frees organically bound fractions) and labile phosphorus (associated with soil particles). Biologically available phosphorus describes a mixture of phosphorus fractions of different availability. Vollenweider (1979) described the following phosphorus sources in terms of decreasing biological availability, which should be considered important in nutrient control measures. These are urban sewage plus certain industrial effluents greater than erosional runoff and leaching from forests and agricultural areas.

16.2.1 Internal Loading of Phosphorus

In suitable conditions at the water sediment interface, nutrients contained in the sediments are released into the water body. In a eutrophic lake, net oxygen consumption occurs in the tropholytic zone below the compensation depth. As alternate terminal electron acceptors are consumed, the redox potential decreases that tends to decrease with greater depth in the water column and in sediments. Once the redox potential of the ferric-ferrous couple is reached (approximately

at 120 mv) (Kortmann and Rich 1994), both soluble ferrous iron and soluble phosphate accumulate. If the redox potential continues to decrease, sulfate is reduced to sulfide at ~75 mv) (Kortmann and Rich 1994), which can remove iron and permanently reduce phosphate binding capacity by interacting readily with ferrous iron to produce ferrous sulfide (FeS). If FeS precipitates to form pyrite (FeS_2), ferrous iron is no longer susceptible to oxidation to ferric iron with the return of aerobic conditions. The relationships among sulfur, iron, and phosphorus binding capacity raises questions about potential impacts from increased sulfate loading by algicide applications (copper sulfate), alum (aluminum sulfate) treatments, and acid rain (sulfuric acid). Holdren and Armstrong (1980) have quoted scientific values of sediment phosphorus release rates from several lakes in the USA regarding aerobic (0–13 mg P/m^2/day) and anaerobic (0–50 [max. 150] mg P/m^2/day) conditions.

16.2.2 Phosphorus Mobilization and Transport

Two different mechanisms are expected to occur simultaneously or within a short time regarding phosphorus mobilization: (1) phosphorus bound to particles or aggregates of particles in the aquatic sediment must be transferred to the pool of dissolved phosphorus in the water and (2) processes which transport the dissolved phosphorus to the lake water must be in order. Important processes regarding phosphorus mobilization are desorption, dissolution, ligand exchange, and enzymatic hydrolysis. These processes are affected by a number of environmental factors, of which redox potential, pH and temperature are the most important ones. Essential phosphorus transport mechanisms are diffusion, wind-induced turbulence, bioturbation, and gas convection. Dissolution and diffusion of phosphorus, controlled by Redox potential, are considered as the dominant mechanisms for phosphorus release from stagnant hypolimnetic bottom areas of water bodies. All the mobilization and transport processes can theoretically contribute to the overall phosphorus release from sediments in shallow lakes. At high temperatures, microanaerobic zones are formed very rapidly, and redox potential controlled liberation of phosphate can occur to well-aerated water. Wind-induced turbulences often have a dominating role among the phosphorus transport processes (Nurnberg 1994).

16.2.3 Nitrogen Transformations

Transformations between various nitrogen compounds in the nitrogen cycle of aquatic ecosystems are important for potential management of lakes. Most phytoplanktons, which create nuisance bloom conditions are capable of nitrogen fixation and are not dependant on combined forms of dissolved nitrogen. Of the combined forms of nitrogen, the most important ones are ammonia and nitrate. Nitrogen fixation, occurring in blue green algae, is inhibited by high content of cellular ammonia that results from decomposition of organic matter. Ultimate sources of ammonia include nitrogen fixation and nitrate assimilation in the aquatic and paralimnetic ecosystem components. Under aerobic conditions, ammonia is first oxidized to nitrite and then to nitrate in a two-step process called nitrification. Under anaerobic conditions, conversion of ammonia to nitrate does not occur and ammonia often accumulates at the bottom of the lakes. Total oxygen demand includes respiratory demand and non-respiratory demand (e.g., chemosynthesis). Nitrate is the first alternate terminal electron acceptor used in anaerobic respiration when oxygen is exhausted. As long as nitrate remains available, the redox potential remains above the threshold value that is required for iron reduction and subsequent release of sediment-phosphorus from ferric hydroxyphosphate complexes present in the sediments. Enhancing nitrification of ammonia to nitrate, and subsequent use of nitrate in denitrification can stabilize the redox potential and reduce internal phosphorus loading.

16.3 Source of Mineral Nutrients in Eutrophication

There are many sources of nutrients causing eutrophication of lakes and other water reservoirs. Water quality of these water bodies is affected directly or indirectly by the anthropogenic activities undergoing in the entire drainage area of the water body. A lake or water reservoir may also be naturally eutrophied owing to nutrient-rich runoff from the agricultural land situated in a fertile area with nutrient-enriched soils. In many lakes and reservoirs, wastewater is the main source of nutrients, as untreated wastewater or the wastewater treated only by conventional mechanical/biological methods still contains nitrogen (25−40 mg L^{-1}) and phosphorus (6−10 mg L^{-1}). Both nitrogen and phosphorus can be removed from water reservoirs using well-known techniques. Phosphorus may be removed by addition of a chemical that precipitates phosphate through a chemical reaction. Nitrogen is usually removed by biological means employing the microbial activities. Removal of nitrogen costs more money and is also technically more difficult compared to phosphorus. Drainage water from agricultural land also contains phosphorus and nitrogen. It usually contains much more nitrogen than phosphorus because phosphorus is usually bound to soil particles. Extensive use of fertilizers results in significant concentrations of nutrients particularly that of nitrogen, in agricultural runoff. If eroded soil reaches the lake, both phosphorus and nitrogen present in the soil

Table 16.1 Classification of lakes according to the extent of the eutrophication. (Source: Janus and Vollenweider (1981)

Parameters	Types of eutrophication			
	Oligotrophic	Mesotrophic	Eutrophic	Hypereutrophic
Average concentration of total phosphorus	8.0	26.7	84.4	>200
Average concentration of total nitrogen	661	753	1875	High
Average concentration of chl-a	1.7	4.7	14.3	>100, range 100–200
Peak concentration of chl-a	4.2	16.1	42.6	<500

All values are expressed as μg L^{-1}

contribute to eutrophication. Wetlands are increasingly used to solve the problem of diffuse pollution from agricultural lands, which causes eutrophication. Both nitrogen and phosphorus may be removed by wetlands. Nitrate is converted to free nitrogen and released to the air in wetlands. This is not harmful, as free nitrogen constitutes about four-fifths of the atmosphere. Phosphorus is removed through its adsorption by wetland soils; it is subsequently taken up by the plants. In addition, it is also necessary to control fertilizer usage in agricultural practices as it may end up in the drainage area; the inflow coming from these drainage areas may cause diffuse pollution. Rain water contains phosphorus and nitrogen owing to air pollution. As nitrogen is more mobile in the atmosphere than phosphorus, it is usually over 20 times more concentrated than phosphorus in the rain water. Nitrogen content of the rain water can only be reduced by efficient control of the air pollution in the entire region. When lakes are used for aquaculture, excessive addition of fish food pollutes the water owing to incomplete use of the fish-food supplied. Nitrogen and phosphorus present in the excess food is dissolved or suspended in the water. The muddy bottom layer (sediment) of lakes contains relatively high concentrations of nitrogen and phosphorus. The nutrients in the sediment originate from settling of algae and dead organic matter. These nutrients are released into water, particularly under conditions of low oxygen concentrations. The nutrients released from sediments are referred to as internal loading of the lake. Lakes and other water reservoirs can be classified according to the extent of their eutrophication levels into four main classes: oligotrophic, mesotrophic, eutrophic, and hypereutrophic (Table 16.1, Janus and Vollenweider 1981). This classification was laid down from extensive examination of eutrophication in countries within the Organization for Economic Cooperation and Development (OECD) in the 1970s and early 1980s. It was based on concentrations of phosphorus, nitrogen, and chlorophyll a; chlorophyll a roughly indicates the concentration of plant biomass (on an average chlorophyll a is 1% of the algae biomass).

16.4 Mineral Nutrients and their Role in Eutrophication

Plants, like all other living things, need food (mineral nutrients, photosynthates, metabolites.) for their growth and development. Plants require 19 essential elements. Carbon, hydrogen, and oxygen are derived from the atmosphere and soil water. The remaining 16 essential elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, zinc, manganese, copper, boron, molybdenum, chlorine, sodium, nickel, and silicon) are supplied either from soil minerals and soil organic matter or by organic or inorganic fertilizers. The sodium is required for C-4 and CAM plants (Subbarao et al. 2003). Silicon is essential for diatoms and members of Equisetaceae (horsetails or scouring rushes); it is semiessential for such important crops as rice and sugarcane (Epstein 2001; Epstein and Bloom 2005; Rains et al. 2006). Plants utilize these nutrients efficiently. Each type of plant is unique and has an optimum nutrient range as well as a minimum requirement level. Below this minimum level, plants start to show nutrient deficiency symptoms. Excessive nutrient uptake can also cause poor growth because of toxicity. Therefore, the proper amount of application and the placement of nutrients are important. Soil and plant tissue tests have been developed to assess the nutrient content. By analyzing this information, plant scientists can determine the nutrient need of a given plant in a given soil. In addition to the levels of plant-available nutrients in soils, the soil pH plays an important role in nutrient availability and elemental toxicity.

16.4.1 Sources and Functions of Nitrogen

Nitrogen (N) is available to plants as ions of nitrate (NO_3^-) and ammonium (NH_4^+). N is biologically combined with C, H, O, and S to form amino acids, which are the building blocks of proteins. Amino acids are used in formation of protoplasm, which is the site for cell division and, thus, for

plant growth and development. Since all plant enzymes are made of proteins, N is needed for all of the enzymatic reactions in a plant. N is a major part of the chlorophyll molecule and is, therefore, necessary for photosynthesis. N is a necessary component of several vitamins. It improves the quality and quantity of dry matter in leafy vegetables and protein in grain crops (Black 1973; Marschner 2002).

16.4.2 Sources and Functions of Phosphorus

Phosphorus (P) is available to plants as orthophosphate ions (HPO_4^{2-} and $H_2PO_4^-$). In photosynthesis and respiration, P plays the major role in energy storage and transfer in the form of ADP (adenosine diphosphate), ATP (adenosine triphosphate), DPN (diphosphopyridine nucleotide), and TPN (triphosphopyridine nucleotide). P is part of the RNA and DNA structures, which are the major components of genetic information in the cell. Seeds have the highest concentration of P in a mature plant; P is required in large quantities in young cells, such as shoots and root tips, where metabolism is high and cell division is rapid. Additionally, P aids in root development, flower initiation, and seed and fruit development. P has also been shown to reduce disease incidence in some plants and improve the quality of certain crops (Raghothama 1999; Marschner 2002; Taiz and Zeiger 2006).

16.4.3 Role of Nitrogen and Phosphorus in Eutrophication

The loading of N and P to the rivers, lakes, and oceans is very strongly influenced by human population densities, the population densities of livestock, and the land use (Omernik 1977; Reckhow et al. 1980; Jones et al. 1984; Cole et al. 1993; Caraco 1995; Howarth et al. 1995, 1996; Jaworski et al. 1997; Smith et al. 1997). Of the many mineral resources required for plant growth, inorganic N and P are the two principal nutrients that have been found to limit the growth of terrestrial plants (Schlesinger 1991; Vitousek and Howarth 1991; Sharpley et al. 2003). However, this nutrient limitation of plant biomass is not restricted to terrestrial ecosystems alone. The supply rate of N and P also strongly influences the growth of algae and vascular plants in the freshwater and marine ecosystem (Vollenweider 1968; Hecky and Kilham 1988; Howarth 1988; Smith 1998). Water bodies having relatively large supplies of nutrients are termed eutrophic (well nourished), and those having poor nutrient supplies are termed oligotrophic (poorly nourished). Waters having intermediate nutrient supplies are termed mesotrophic.

The concept of nutrient limitation can be considered the basis of eutrophication research. It implies that: (1) one key nutrient should be the primary limiting factor for plant growth in a given ecosystem, (2) the growth of plants in a given ecosystem should be proportional to the rate of supply of this key nutrient, and (3) the control of eutrophication should be accomplished by restricting the loading of this key nutrient to the ecosystem (Smith 1998). Nitrogen is an element that can limit algal biomass in natural waters. The forms of nitrogen that are generally available for aquatic plant growth are nitrate and ammonia. In addition, certain algae and bacteria in natural waters can use dissolved nitrogen gas as the nitrogen source. Normally, ten times as much nitrogen is required as phosphorus for growth of algae (on a mass basis). Natural water bodies typically contain at least this relative quantity of algal-available nitrogen over phosphorus. During the past decades, several techniques have been developed to assess the relative significance of nitrogen versus phosphorus as growth-limiting elements for algae in natural waters. These include algal assay procedures and examination of changes in concentrations of available nutrient forms during algal blooms. According to these procedures, generally freshwater lakes tend to be phosphorus-limited, while marine waters tend to be nitrogen-limited. There are exceptions to the generalizations, which are usually associated with gross pollution of the water body owing to the activities of man, such as from agricultural drainage and discharge of domestic wastewaters. Although phosphorus may not be limiting the algal growth in general because of large phosphorus inputs, the control of phosphorus inputs can decrease the available phosphorus concentration in a water body, making the phosphorus limiting in a water body. For most freshwater bodies, there is sufficient evidence to conclude that phosphorus is the major limiting element for aquatic plant growth. Nitrogen ranks the second in this regard. Because the influence of the human activities, excessive nitrogen, phosphorus, and other nutrients are loaded into water bodies like lake, reservoirs, embouchure and bay, which result in the fast growth of algae and other planktons that deteriorate the water quality (Western 2001). Although nitrogen and phosphorus exert primary control over the growth of total algal biomass in most surface waters, trace elements, vitamins, and organic growth factors may also control the types of algae present. The relative roles of nitrogen and phosphorus in the eutrophication process are usually reversed from those typically found in fresh water.

In conditions of restricted circulation and massive nutrient inputs, more or less classical eutrophication problems do occur in marine water. In such situation, there may be a large growth of algae. Eventually, the algae die and subsequently settle through the thermocline. Decomposition of the dead algae depletes the oxygen in the bottom area of the water bodies. The depletion of dissolved oxygen results in large-scale destruction of benthic organisms in the area, many of which may be of great commercial importance, including lobster, crabs, flounder, and other flat fish. In this case nitro-

gen becomes the limiting element. Nutrient loading to lakes, estuaries, and coastal oceans has greatly increased through human activities over the past few decades, increasing the rate of transformation (eutrophication) of aquatic ecosystem (Bishop et al. 2006). There are different views on the relationship of nutrient enrichment to water eutrophication and formation of algal bloom such as (1) When P concentration in water is low, it may be the limiting factor for inducing water eutrophication and algal bloom formation; (2) When P concentration in water increases rapidly, other factors may become new limiting factors, such as pH, water depth, temperature, light, wave, wind, or other biological factors; (3) The influence of N and P lasts for a longer time because of the high development level of our society (Zhao 2004). N and P input and enrichment in water are the primary factors to induce water eutrophication. Based on the chemical components of algae, the simulated molecular formula of algae may be as follows: $C_{106}H_{263}O_{110}N_{16}P$. The formula indicates that N and P are the elements which account for least proportion in the molecular formula of algae, especially P, which is the main limiting factor to control the growth of algae in water (Mainstone and Parr 2002). It was reported that 80% of the lake and reservoir eutrophication is restricted by phosphorus, about 10% of the lake and reservoir eutrophication is related to nitrogen, and the rest 10% of the lake and reservoir eutrophication is related to other factors (Zhao 2004). In many ecosystems, phytoplankton biomass is correlated with the availability of N or P (Cloern 2001; Bledsoe et al. 2004). The composition of phytoplankton species is also affected by the concentrations of N and P (Reynolds 2006). The N:P ratio (Redfield ratio) in the water body is an important indicator that points out which nutrient is limiting for algal growth (eutrophication). If the Redfield ratio is 16:1, P is most likely the limiting factor for algal growth; while, lower ratios indicate that N is of great importance (Redfield et al. 1963; Hodgkiss and Lu 2004). Furthermore, P has been shown to be the principal limiting nutrient for primary production of phytoplankton in many freshwater bodies (Philips 2002; Sharpley et al. 2003), while N is commonly limiting in marine ecosystems (Cloern 2001). Nonetheless, there are many exceptions to this general pattern. In some freshwater environments, particularly in the tropics and subtropics, N has been found to be the primary limiting nutrient for phytoplankton production, owing to excessive P load and long growing seasons. For instances, in the Ten Mile Creek of Indian River Lagoon, where total P is >0.2 mg L^{-1}, chlorophyll-a and turbidity sharply increased with addition of available N (0.2~6.0 mg L^{-1}), but is not affected by addition of reactive P species (Lin et al. 2008). The results indicate that available N is the limiting nutrient for the growth of phytoplankton at water bodies with high P. In phosphate-deficient water bodies or those having reasonably good growth of blue-green algae, which fix enough of the atmospheric nitrogen, phosphorus becomes the limiting element, because a portion of P is used to counterbalance high nitrate content (Reynolds 2006). In such circumstances, no algal boom may arise in heavily eutrophicated water bodies carrying high content of both N and P. Thus, it is the key point to control the concentrations of both N and P reasonably for solving the problem of water-eutrophication. Further, the abundance, composition and geographical and periodic distribution of phytoplanktons in a water body vary with the variations in the chemical composition of natural waters. It is believed that the growth of phytoplankton is influenced by dissolved silicate-Si (DSi) concentration in water and its ratio to nitrate (DSi:nitrate-N). When the DSi:nitrate-N atomic ratio is near 1:1, aquatic food webs associated with diatoms (which require silicate to flourish) may thrive and the frequency or size of harmful or noxious algal blooms may increase. In fact, the DSi:nitrate-N ratio and nitrate-N concentration are the stout comparative indicators of eutrophication in large rivers (Turner et al. 2003).

16.4.4 Sources and Functions of Potassium

Potassium (K) is available to plants as potassium ion (K^+). Unlike N and P, K does not form any vital organic compounds in the plant. However, the presence of K is vital for plant growth because K is known to activate many enzymes necessary for metabolism. Furthermore, K assists in regulating the plant's water-use by controlling the opening and closing of leaf stomata, where from water is evaporated to cool the plant. In photosynthesis, K has the role of maintaining the balance of electrical charges at the site of ATP production in photosynthesis. K promotes the translocation of photosynthates (sugars) for plant growth or storage in fruits or roots. Through its role in assisting ATP production, K is involved in protein synthesis. K has been shown to improve disease resistance in plants, increase the size of grains and seeds, and advance the quality of fruits and vegetables (Usherwood 1985; Marschner 2002; Lester et al. 2010).

16.4.5 Role of Potassium in Eutrophication

Potassium constitutes approximately 1% of the dry weight of the microbial cell. As the cofactors for some enzymes, potassium and magnesium stimulate enzyme reactions associated with a synthesis of cell materials (Brdjanovic et al. 1996). The role of potassium in microorganisms responsible for biological phosphorus removal is even more important. Potassium functions in cell membrane permeability and plays major role in phosphate transport between surrounding environment and the cell (Medveczky and Rosemberg 1971). Moreover this cation is an essential counter ion for

polyphosphate in the cell, and is generally an important factor in the cells energy generation (Buffle 1990; Bianchi et al. 1995). Enzyme, polyphosphate kinase catalyzes polyphosphate biosynthesis in the presence of magnesium ions by transferring the terminal phosphoryl group from ATP to polyphosphate chain. Polyphosphate degradation is driven by several enzymes which depend on inorganic cations. Magnesium acts as an important counter ion of polyphosphates too. It is taken up and released simultaneously with phosphate. Therefore, these cations (potassium and magnesium) are necessary for polyphosphate accumulation and biological phosphorus removal. Potassium ions strongly inhibit the growth of *Microcystis* and thus offer a new possibility for the regulation of *Microcystis* blooms. Potassium ions, added as either chlorides or bicarbonates, inhibit the growth of *M. flosaquae* C3-9 and *M. aeruginosa* both found in pond water and defined media, whereas comparable sodium salts at the same concentrations do not inhibit *Microcystis* growth. Parker et al. (1997) studied the samples from five ponds that were alkaline and eutrophic and contained more than 2.8 mM of potassium, but none of the ponds had detectable *Microcystis* growth. It is, therefore, possible that the potassium concentration in the studied ponds did not influence the prevalence of *Microcystis*. They collected the aliquots of KCl-supplemented and unsupplemented pond-water inoculated with either *M. aeruginosa* alone or a mixture of *M. aeruginosa* and *Wolffia arrhiza*. In both the cases, the addition of KCl, but not NaCl, inhibited the growth of *M. aeruginosa*. In the second case, *W. arrhiza* predominated in KCl-supplemented aliquots but *W. arrhiza* did not flourish in unsupplemented or NaCl-supplemented aliquots. These observations indicate that the addition of KCl is sufficient to alter the prevalence of *M. aeruginosa* in pond water. The high-potassium and low-potassium ponds probably differed in other properties as well, but the potassium effect was dominant. Zehnder and Gorham (1960) achieved the greatest yield of *M. aeruginosa* NRC-1 in modified Fitzgerald medium that contained one-half or one-fourth of the usual KH_2PO_4 concentration and that exhibited Na/K ratios of 9–15. Potassium toxicity to *Microcystis* at these concentrations is unexpected, since K^+ is the major cation inside cells. The cause of potassium sensitivity of *Microcystis* is unknown, but several plausible explanations involve potassium inhibition through sodium-related phenomena. For example, most *Microcystis*-containing ponds are contaminated with detergents and soaps used for laundry and bathing. Potassium-based instead of sodium-based detergents and soaps would be less likely to promote *Microcystis* blooms. Because the potassium concentrations that are toxic to *Microcystis* are not harmful to most other organisms, potassium compounds may be a safer alternative to copper sulfate or to other biocides that are currently added to water supplies to limit *Microcystis* blooms. The amounts of potassium that would have to be added might be excessive for large lakes with rapidly flowing water. The manipulation of potassium concentrations might affect the amount of *Microcystis* waters, which are extensively used by humans and domestic animals. Potassium does not decrease the growth of the duckweeds in pond water and probably would not affect most types of true algae. Although duckweeds and algae can be nuisances, they do not produce microcystins (Carmichael 1992; Runnegar et al. 1995) or other toxic products of *Microcystis* (Bianchi et al. 1995; Sellner 1997; Guo et al. 1999; Packard et al. 2000). Microcystins are cyclic nonribosomal peptides produced by cyanobacteria such as *Microcystis aeruginosa*. They can be very toxic for plants and animals including humans.

16.4.6 Sources and Functions of Calcium

Calcium (Ca) is available to plants as the calcium ion (Ca^{2+}). Ca has a major role in the formation of cell wall and maintaining its plasticity, affecting normal cell division by maintaining cell integrity and membrane permeability (Hirschi 2004). Further, Ca is an activator of several enzyme systems used in protein synthesis and carbohydrate transfer. Ca combines with anions including those of organic acids, sulfates, and phosphates. It acts as a detoxifying agent by neutralizing organic acids in plants. Ca is essential for seed production in plants such as peanut. Ca indirectly assists in improving crop yields by reducing soil acidity when soils are limed (Uchida 2000; Marschner 2002).

16.4.7 Role of Calcium in Eutrophication

Biogenic calcium carbonates, calcite, and aragonite, are major components of the sediments and of the suspended matter in the water bodies. The adsorption and coprecipitation of phosphate on the suspended matter may play an important role in the cycling and transport of nutrients in water bodies. The release of phosphate from the suspended matter may be the source of phosphorus for the onset and sustenance of the algae bloom. Previous studies have shown that phosphate is strongly adsorbed on the surface of calcite and aragonite (Gaudette and Berrylyons 1980). This adsorption has been used to explain why calcium carbonate-rich sediments contain low concentrations of dissolved phosphate in their pore waters. An understanding of the carbonate system in the water bodies is important to determine the uptake of inorganic carbon by phytoplankton and the saturation state of calcite and aragonite particles that can adsorb phosphate. The carbonate system can be characterized by measuring the variables that control the carbonate system (pH, TA, total alkalinity; TCO_2, total carbonate; and pCO_2, the partial pressure of CO_2; Millero 1995). The carbonate system can be

affected by precipitation and dissolution of calcium carbonates and the production and destruction of phytoplankton. Measurements of pH are also important in understanding the dynamic nature of biogeochemical processes and the state of all the acid-base systems present in the water. The eutrophication-induced phytoplankton bloom, hence the intensive photosynthesis, can locally decrease the pCO_2 and increase the pH. The precipitation of calcium carbonate may occur at this high pH in seawater already supersaturated with respect to calcium carbonate (Berner and Morse 1974). The precipitation of calcium carbonate has been reported to be triggered by phytoplankton blooms in some shallow lakes. This suggests that the precipitation of calcium carbonate, caused by phytoplankton blooms, may play an important role in the cycling and transport of nutrients in water bodies through adsorption and coprecipitation of nutrient compounds (e.g., PO_4^{3-} and NH_4^+) on the suspended matter. Studies are needed to examine how the inorganic formation of calcium carbonate can control the fate of nutrients in water bodies produced by anthropogenic activities. The model would require the knowledge of partitioning of phosphorus between different reservoirs, such as a water column, suspended matter, and sediment; the speciation of phosphorus in each reservoir (organic and inorganic phosphorus) and their biological availability; the influence of pCO_2, total CO_2, pH, salinity, temperature, and other environmental factors on the phosphorus transformation between different reservoirs (Burton and Walter 1990).

16.4.8 Sources and Functions of Magnesium

Magnesium (Mg) is available to plants as the magnesium ion (Mg^{2+}). The predominant role of Mg is as a major constituent of the chlorophyll molecule, and it is therefore actively involved in photosynthesis. Mg is a cofactor in several enzymatic reactions that activate the phosphorylation processes. Mg is required to stabilize ribosome particles and also helps stabilize the structure of nucleic acids. Mg also assists the movement of sugars within a plant (Uchida 2000; Marschner 2002).

16.4.9 Role of Magnesium in Eutrophication

Magnesium is often associated with calcium in all kinds of waters, but its concentration remains generally lower than the calcium (Venkatasubramani and Meenambal 2007). Magnesium is essential for chlorophyll synthesis and acts as a limiting factor for the growth of phytoplankton (Dagaonkar and Saksena 1992). Therefore, depletion of magnesium reduces the phytoplankton population. Dwivedi et al. (2000) recorded magnesium content up to 3.27 mg L^{-1} in Naktara reservoir. In the present investigation, the magnesium content up to 5.60 mg L^{-1} was observed with higher concentration during winter season and lower concentration in monsoon season. At neutral to alkaline pH, magnesium ions are capable to restrict the tendency to precipitate of phosphorus (Stratful et al. 2001). Being the essential element, magnesium often limits the growth of primary producers such as algae, other aquatic plants, cyanobacteria, photosynthetic bacteria. Some heterotrophic microorganisms are also capable of solubilizing phosphates combined with calcium or magnesium (Atlas and Bartha 1998). These soluble forms can be readily taken up by plants, algae, cyanobacteria, and autotrophic bacteria and is assimilated into organic cellular components (DNA, RNA, ATP).

16.4.10 Sources and Functions of Copper

Copper (Cu) is available to plants as copper ion (Cu^{++}). Cu is essential in several plant enzyme systems involved in photosynthesis. Cu is part of the chloroplast-protein plastocyanin, which forms part of the electron transport chain. Cu may have a role in the synthesis and/or stability of chlorophyll and other plant pigments (Uchida 2000; Marschner 2002).

16.4.11 Role of Copper in Eutrophication

Copper is a phytotoxic heavy metal (Rai et al. 1981) and it inhibits the photosynthesis and growth of algae at low concentrations (Garvey et al. 1991). Plant communities grown in high phosphate concentrations were more tolerant to copper than the ones grown in lower phosphate concentrations (Guasch et al. 2002). An increase in the tolerance to copper was also observed after phosphorus addition in the soil with low phosphate concentrations (Guasch et al. 2002). Several arguments have been proposed in order to understand the interaction between phosphorus availability and copper toxicity. In general, biofilm-matrix plays an important role in metal tolerance, as the biofilm-matrix can have a protective function by limiting the penetration of metals (Barranguet et al. 2002; Guasch et al. 2003). It has been suggested that Cu induces the deficiency of P (Nalewajko and Olaveson 1994). Communities growing with higher P availability may be more tolerant to copper owing to the possible formation of polyphosphate bodies that can complex the copper and detoxify the cells (Hall et al. 1989). Copper toxicity in natural periphyton communities depends on phosphorus availability (Guasch et al. 2004). Verma et al. (1993) evidenced that Cu toxicity in cyanobacteria was owing to Cu-induced phosphate starvation and that the exogenous addition of phosphate could antagonize the Cu-effect in *Nostoc calcicola*. It has been reported that Cu induces the deficiency of P

directly by the inhibition of phosphate uptake and indirectly by reducing the permeability of cell membranes (Nalewajko and Olaveson 1994). Hall et al. (1989) also found greater Cu toxicity in P-limited cultures of *Chlorella vulgaris*. They concluded that P-limited cells were more sensitive to Cu, owing to impaired metal exclusion/elimination mechanisms produced by P-limitation. The pH of the media has been considered an important factor influencing the toxicity of Cu on periphyton (Guasch et al. 2002) and on algal cultures (Stadorub et al. 1987). These authors showed an increase in Cu toxicity when pH was reduced. This can be explained by Cu speciation, because the amount of Cu^{2+} (which is considered the most available form of Cu for algae) increases at lower pH (Guasch et al. 2002). Cu toxicity was progressive by indiscriminately damaging the algae at or protruding biofilm surface to deeper biofilm layers; thus, the magnitude of the effect depended on the initial biomass in the short term (Guasch et al. 2004).

16.4.12 Sources and Functions of Iron

Iron (Fe) is available to plants as iron ions (Fe^{2+} or Fe^{3+}). Fe is essential in the heme enzyme system in plant metabolism (photosynthesis and respiration). The enzymes involved include catalase, peroxidase, cytochrome oxidase, and other cytochromes. It is part of protein ferredoxin and is required in nitrate and sulfate reductions. Fe is also essential in the synthesis and maintenance of chlorophyll in plants and is strongly associated with protein metabolism (Uchida 2000; Marschner 2002).

16.4.13 Role of Iron in Eutrophication

Besides nitrogen and phosphorus, iron should also be considered important regarding the regulation of eutrophication in lakes. The fluctuation in iron concentration may have an important influence on the metabolic activity of the algal cells, and the spectral characteristics of algae could reflect the physiological features of algae. Studies of algal spectral properties under different iron supply would be meaningful for determining the algal bloom and for developing the remote sensing warning system of lake eutrophication. Iron reduction leads to the release of both Fe- and Fe-bound P, and sulfate reduction forms toxic H_2S gas, which is capable to reduce the Fe oxides efficiently, leading to blocking of Fe cycling. Iron reacts with sulfide to produce the virtually insoluble precipitate of ferrous sulfide (FeS). It was postulated that iron might function as an efficient scavenger of sulfide, which would prevent it from reaching the toxic concentrations. In contrast, oxygen production by the microphytobenthos may result in iron oxidation. Ferric iron (Fe^{3+}) is known to form an insoluble complex with phosphate. Thus, iron may also play a role in regulating the availability of phosphate for algal growth. However, the mechanisms of iron immobilization and mobilization are not precisely known. The bulk of iron is present as ferrous sulfide which is virtually insoluble. Benthic microorganisms such as cyanobacteria may also bind with and accumulate iron (Stal 1994). Thus, immobilization of iron may be associated with microbial activities such as (i) sulfate- and sulfur reduction, which produce the sulfide that will precipitate as FeS, (ii) oxygenic photosynthesis by microphytobenthos that produce the oxygen that will oxidize iron and form insoluble iron hydroxides either chemically or biologically, (iii) binding to extracellular polysaccharide sheaths of benthic microorganisms (e.g., Cyanobacteria; Decho 1990). Mobilization and liberation of the iron from the sediments is, therefore, possible when the activities described above cease. When acid volatile sulfide is subsequently oxidized (chemically and/or biologically) iron will be liberated. Ferrous iron (Fe^{2+}) (when not precipitated as metal sulfide) is very soluble and this might explain the mobilization and dissolution of iron from the sediment, which would be most pronounced in the surface layer. Oxygen produced by the Cyanobacteria may precipitate the ferric iron and, therefore, these organisms have also been shown to accumulate iron in their extracellular polysaccharide sheath (Stal 1994). Ferrous iron reacts instantaneously with oxygen. Ferrous iron has also been reported as a possible electron donor for cyanobacterial photosynthesis (Cohen 1989).

16.5 Impact of Eutrophication on Aquatic Life

Phosphates and nitrates occur in small amounts in all aquatic environments. They are required to maintain the growth and metabolism of aquatic plants and animals. However, excessive amounts of these minerals can prove to be quite harmful for aquatic life. From different sources, dissolved minerals and nutrients flow into streams, lakes, and other water bodies. A good portion of these dissolved minerals consists of phosphates and nitrates. Levels of phosphates and nitrates, which are intolerable to aquatic organisms, result in depletion of dissolved oxygen levels by causing algal blooms. Inflow of high amounts of phosphates and nitrates to water bodies (eutrophication), is the main cause in the destruction of lake ecosystems around the world (Khan and Ansari 2005). Several scientists have studied mineral levels in different water bodies, concluding that the levels of phosphates and nitrates adversely affect the overall health of the water and its inhabitants (Yanamadala 2005). Excessive accumulation of nutrients (specifically those of phosphates and nitrates) cause luxuriant growth of algae and bacteria in water bodies. It also causes a burst of growth in other aquatic plants and phytoplankton, forming a layer of green slime across the

surface of water bodies. This layer inhibits light and oxygen movement into the water. Plants below the surface of water may die owing to lack of light, which result in the decay and decomposition of these plants, turning the water foul-smelling and turbid. The loss of oxygen from the water causes aerobic organisms to suffer, while anaerobic organisms are flourished. Moreover, fishes die from the loss of oxygen, and the total water quality of the water is lowered as the balance of life is disturbed. Eutrophic water is often scummy, cloudy, soupy-green in color, and overgrown with algae and other aquatic plants. Algal blooms, resulting from phosphate and nitrate addition in water bodies may end owing to harsh environmental factors; the resulting decay of the algae often leads to the growth of disease-causing bacteria.

Increased levels of phosphates and nitrates often indirectly harm the environment by causing bacterial growth and huge algal blooms (Khan and Ansari 2005; Yanamadala 2005). The study based on water bodies in Municipal Golf Course, located in Austin (USA) revealed that the runoff of chemicals used to treat the turf grass included significant amounts of phosphates and nitrates. The data showed that the nitrates were in much higher concentration during the winter months owing to increased rainfall, turf grass dormancy, and decreased microbial and bacterial activity. Phosphate levels were not as affected as those of nitrates by the seasons. However, the phosphate levels coming from the drainage system were significantly higher than those of most agricultural runoff sources. This could potentially cause great harm to nearby surface water systems and the many diverse organisms that inhabit those (Balogh et al. 2006).

Another study is based on Harbor Lake Machado, which is located near Los Angeles (USA). Many unique biological species have their home in the lake, and hundreds of migratory birds visit it annually. While organizations do their best to clean the water of Lake Machado, pollutants (large levels of phosphates and nitrates) continue to pour in from storm drains and agricultural runoff, which most likely account for the rise in bacterial and algal growth in the lake. The phosphate and nitrate levels are well beyond standard safety limits set by the U.S. Environmental Protection Agency. Pollution of water bodies is almost entirely the fault of humans and industrialization. Hence, Lake Machado is becoming increasingly dangerous for animals and plants inhabited there. If high-mineral content runoff continues to pour into the water body, the quality of water-dwelling organisms and that of the water itself will continue to decline (Engel et al. 2006). At present, the techniques such as resin-based system, adopted by Storm-water Management of Portland (USA), are being developed to reduce the pollution that goes into important water bodies. This technique removes the dissolved phosphorus from storm-water runoff (Kreuzer 2000).

16.6 Conclusions

Generally, nitrogen and/or phosphorus are less abundant in water than other elements needed, relative to their composition in plants. About eight times more nitrogen is required than phosphorus in algal bloom formation. Phosphorus, thus, limits eutrophication if nitrogen is more than eight times as abundant as phosphorus, while nitrogen limits eutrophication if its concentration is less than eight times as abundant as phosphorus. Untreated wastewater and wastewater treated by mechanical/biological methods contain about 32 mg L^{-1} of nitrogen and about 8 mg L^{-1} of phosphorus, on an average. In a lake, heavily loaded with wastewater, eutrophication is limited by nitrogen, as the nitrogen concentration in the discharged wastewater is only four times the phosphorus concentration. Such lakes often display extensive blooms of blue-green algae as unsightly surface scum. Some species of blue-green algae use nitrogen directly from the air and grow, although dissolved nitrogen is limiting. Lakes that receive natural tributaries and drainage water from agriculture, however, have high nitrogen concentrations and are therefore usually limited by phosphorus. The central question is not to determine which nutrient is limiting but to determine which nutrient can most easily be made limiting. As phosphorus is more easily and less expensively removed from wastewater than nitrogen, in many cases (but not all) the best environmental management strategy for lakes and reservoirs is to remove as much phosphorus as possible from wastewater.

It has been established that detergents, domestic sewage, and fertilizers are the three major human made sources of nutrient enrichment in the eutrophication of natural water bodies. Water bodies located near large cities are likely to receive more phosphorus from domestic effluents containing detergents. It is worth cautious, and in most cases essential, to implement a dual-nutrient reduction strategy while developing measures to control eutrophication. A focus on only P or N reduction should not be considered unless there is clear evidence or strong reasoning that a focus on only one nutrient is justified in that ecosystem and will not harm downstream ecosystems. The technologies for wastewater treatment to reduce P versus N differ markedly, and reducing atmospheric N deposition does not affect P inputs to aquatic ecosystems. Alleviation of eutrophication in aquatic ecosystems along the land–ocean continuum requires a balanced and strategic approach to control both nutrients appropriately. It is very necessary that some effective control measuring and useful steps, including consciousness programs pertaining to the present threat to water resources on the blue planet need to be employed. Many countries also try to remove nutrient pollution from their waters, and they may use other measures to create eutrophication buffer zones, preventing the spread of the problem.

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Phytoremediation Systems for the Recovery of Nutrients from Eutrophic Waters

17

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Abstract

Eutrophication and availability of freshwater for human consumption is one of the main issues in front of the environmentalists. Eutrophication, acidification, and contamination by toxic substances are posing a threat to the freshwater resources and ecosystems. The consequence of anthropogenic-induced eutrophication of freshwater has resulted in severe deterioration of surface water. Effective control measures need to be taken in order to control eutrophication and restore eutrophic water bodies. In this row, phytoremediation is emerging as a simple low-cost clean up technology for wastewater. Phytoremediation is defined as the engineered use of green plants to remove, or render harmless, various environmental contaminates such as inorganic and organic compounds. Development of aquatic plant systems for nutrient recovery from eutrophic water is essentially required to control eutrophication. The performance of phytoremediation system depends upon many factors such as growth performances of the plants selected for phytoremediation, their nutrients removal potential, efficiency to grow in experimental environment. In order to develop high-efficient nutrients phytoremediation systems aquatic plant species in combinations (mono, bi, tri species culture) can be used. Sufficient work has been done and huge amount of capital is invested so far for the restoration of some major water bodies that are falling under direct threat of eutrophication but the results are unsatisfactorily.

Keywords

Aquatic plants · Phytoremediation · Eutrophication · Environmental factors

17.1 Introduction

The problem of eutrophication and availability of freshwater for human consumption is one of the important issues that requires public attention. Eutrophication, acidification, and contamination by toxic substances have become a threat to the freshwater resources and ecosystems (Johanson et al. 2001). The consequence of anthropogenic-induced eutrophication of freshwaters has resulted in the contamination of surface water which in turn has raised the brows of environmentalist across the world.

The work on eutrophication was started by Vollenweider in 1968 and Rohlich in 1969 (Vollenweider 1968; Rohlich 1969). An enormous number of books, research papers, and articles have been published so far on water pollution, eutrophication, and related management issues (Ansari et al.

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2011a; OECD 1982; Henderson-Sellers and Markland 1987; Ryding and Rast 1989; Harper 1992; Thornton et al. 1999). It is now evident that the nutrients are primarily responsible for limiting productivity in lakes and rivers, which are well-known as the limiting nutrient controversy (Likens 1972). Scientists working on fresh waters have mainly concentrated on phosphorus as a key element in controlling eutrophication. The consequences of cultural eutrophication caused by excessive inputs of phosphorus and nitrogen are:

- Increase in biomass of phytoplankton and macrophytes
- Domination of algal bloom forming species which is toxic to consumers of eutrophic ecosystem
- Change in species composition of macrophyte vegetation and increase in biomass of consumer species owing to increase of biomass of benthic and epiphytic algae
- Frequent fish kills
- Decline in species diversity of aquatic ecosystem
- Decrease in harvestable fish biomass
- Decrease in water transparency
- Anoxic conditions in the aquatic ecosystem
- Problems related to the quality of water and its aesthetic value

The empirical models describe the declining inlake concentrations of chemical elements; especially phosphorus which results in reoligotrophication (Jeppesen et al. 2005; Jensen et al. 2006). The water bodies can be divided into various trophic levels such as autotrophic, nutrient-regulated heterotrophic, and external carbon-controlled state. The autotrophic state in flowing waters depends mainly on phosphorus and nitrogen levels. Algal biomass is positively correlated to gross primary production in streams and rivers (Dodds 2006).

In addition to increasing scientific knowledge, answers to the questions related to eutrophication can influence strategies for ecosystem restoration or rehabilitation (Hecky 2009). Initially, P and C has drawn the attention of limnologists and ecologists as primary causes of eutrophication. However, now it is proved that N also contributes in increasing eutrophication especially in estuaries where it is a limiting factor under normal conditions. Therefore, now it is evident that N is a primary cause of eutrophication in many coastal ecosystems (Paerl et al. 2003).

17.2 The Global Scenario

Most of the countries of the world have now realized the serious threat posed by eutrophication. The water bodies of countries such as India, China, Bangladesh, Pakistan, Indonesia, Switzerland, Poland, Austria, Denmark, Croatia, Ireland, France, Greece, Estonia, Russia, Italy, Turkey, Japan, and the great lakes states of the USA and Canada are under the direct threat of eutrophication (Ansari 2005). In the mid-twentieth century, eutrophication had been recognized as one of the causative factors of pollution in European and North American lakes and reservoirs. Since then, it has become more widespread and surveys showed that 54 % of lakes in Asia, 53 % in Europe, 48 % in North America, 41 % in South America, and 28 % in Africa are in eutrophic state (Colin et al. 2007). In Spain 80 % of the lakes, 70 % of the reservoirs and 60 % river sites were eutrophic in the 1990s with hypertrophy increasing downstream (Alvarez-Cobelas et al. 2001).

A number of lakes and water reservoirs in China are in eutrophic state. The main pollution indicators of these lakes were TN (total nitrogen) and TP (total phosphorus) as recorded by China lake database, CAS Nanjing Institute of Geography and Limnology, searched in April 2009 (CAS 2009). Eutrophication has become a threat to floral and faunal diversity in the coastal areas that are receiving direct input of nutrients from some of the major rivers like the Amazon, Nile, Ganges, Mississippi, Brahmaputra, and Thames. (Khan and Ansari 2005).

17.3 Aquatic Plant Diversity in Eutrophic Ecosystems

Eutrophication causes undesirable changes in species composition of an aquatic ecosystem (Romermann et al. 2008). Acidification and eutrophication have been identified as the two major threats to the survival of aquatic ecosystems which are also causing potentially severe changes to plant diversity (Murphy et al. 2003). The plant species play a vital role in the functioning of soft water lake ecosystems. Lake area, altitude, trophic state, and water quality have been found directly related with the macrophyte species richness. The global changes in the plant diversity of soft water lake in northern Europe are potentially severe (Murphy 2002).

An aquatic system takes thousands of years to become eutrophic which is a natural process. However, a high rate of input of nutrients because of anthropogenic activities significantly enhance the condition in a very short period of time. This is called an artificial eutrophication. The high-nutrient concentrations enhance the excessive growth of phytoplankton and macrophytes in aquatic ecosystem (Rovira and Pardo 2006). Eutrophication causes an increase in plant and animal biomass, frequency of algal blooms, growth of rooted plants and decreases the species diversity which further results in high degree of competition. The high chemical or physical stress also enhance the struggle for survival in eutrophic systems. As a result the diversity of organisms declines in eutrophic than in oligotrophic systems (Ansari 2005).

17.4 Biological Measures (Phytoremediation) to Control Eutrophication

Effective control measures need to be emphasized in order to control eutrophication and restore eutrophic water bodies. Phytoremediation is a simple, low-cost emerging clean up technology for wastewater. It is defined as the engineered use of green plants to remove, or render harmless, various environmental contaminates such as inorganic and organic compounds. Development of aquatic plant systems for the recovery of the nutrients from eutrophic water is essentially required to control eutrophication **(**Ghaley and Farag 2007; Kim and Owens 2010).

The aquatic plants like *Eichhornia crassipes* and *Salvia auriculata* are very efficient to remove nutrients and can be used to reduce the eutrophication processes (Petrucio and Estaves 2000). Water hyacinth is reported for its efficiency to remove about 60–80 % nitrogen (Fox et al. 2008) and about 69 % of potassium from water (Zhou et al. 2007). The roots of water hyacinth were found to remove particulate matter and nitrogen in a natural shallow eutrophicated wetland (Billore et al. 1998). There are many other aquatic plants like *Typha, Phragmites,* and *Glyceria* species that are reported to remove nutrients from eutrophic water (Beltman et al. 1990).

The planted floats are used to remove dissolved phosphorus from irrigation drainage channel. These floats are designed to implement horizontal spreading of aquatic plants on the surface of irrigation drains, fields, or treatment ponds. In the float technology the creeping stems of water plants were utilized to remove soluble reactive phosphorus from the water column (Wen and Recknagel 2002). The seaweeds can also be used to remove the nutrients. Mass culture of commercially valuable seaweed species has been suggested to play an increasingly important role as a nutrient removal system to alleviate eutrophication problems owing to fed aquaculture. Three species of estuarine macroalgae (*Ulva rotundata, Enteromorpha intestinalis* and *Gracilaria gracillis*) were used as biofilters for the removal of phosphate from the effluent of a sea bass (*Dicentrachus labrox*) (Martinez et al. 2002).

There are number of aquatic weeds like *Lemna, Spirodela, and Eichhornia* that were shown to be very efficient in removing nutrients from eutrophic waters if used in controlled environmental conditions (Ansari and Khan 2008, 2009b, 2011). Periphyton removes phosphorus in shallow freshwater ecosystem. The phosphorus removal process includes its uptake, deposition, and filtering from the water (Dodds 2006). Cultures of duckweed *(Lemna minor)* cultivated in the laboratory under controlled environmental conditions remove 7 % of nitrogen and 10 % of the phosphorus by the plant uptake over the 14-day period of operation (Smith et al. 2004; Smith 2007).

17.5 Limiting Factors for the Nutrients Phytoremediation Systems

Nutrients removal capacity of plants and microorganisms in natural and manmade eutrophicated aquatic ecosystems depend on many factors, including retention time, season, temperature, pH, diversity of species, nutrients loading, hydraulic regimes, plant harvesting, light intensity. Nutrients removal efficiency by duckweeds was shown to be varied from plant to plant (El-Shafai et al. 2007). The growth and nutrient removal potential of aquatic plants are affected by many factors such as temperature, water salinity, and physiological limitations of the plant (Ansari and Khan 2009b). Low temperature, high concentration of salts, and low concentration of nutrients may also reduce the performance of aquatic plants in removing nutrients (Lu et al. 2010). The performance of phytoremediation system depends upon the growth performances of the plants selected for phytoremediation, their nutrients removal potential and efficiency to grow in experimental environment. In order to develop high-efficient nutrients phytoremediation systems aquatic plant species in combinations (mono, bi, tri species culture) can be used.

17.5.1 Plant Material

Various common aquatic plant species can be tested singly and in combinations (mono, bi, tri species culture) to develop phytoremediation systems for the recovery of nutrients from eutrophic waters.

17.5.2 Best/Worst Performers Among Plant Species

Among a range of plant species, highest nutrients recovery rates were exhibited by water hyacinth (*Eichhornia crassipes*) and water lettuce (*Pistia stratiotes*) (Polomski et al. 2009). Planted in microcosms, *Carex lacustris* was shown to be the least efficient plant in comparison with *Scirpus validus*, *Phalaris arundinacea,* and *Typha latifolia* (Picard et al. 2005). Highest nutrients recovery rates were found to be exhibited by *Thalia geniculata* and *Oenenathe javanica* in comparison with *Phyla lanceolata* (Polomski et al. 2008).

17.5.3 Species Mixture

Typha significantly outperformed *Juncus* and *Scirpus* both in growth and in effluent quality improvement in small-scale constructed wetlands receiving primary treated wastewater. There was also some evidence that the species mixture outperformed species monocultures (Coleman et al. 2001).

Table 17.1 Aquatic macrophytes used in phytoremediation systems for eutrophic waters

S. no.	Plant name	Worker and year
1	*Eichhornia crassipes*	Petrucio and Estaves 2000; Zhou et al. 2007; Billore et al. 1998
2	*Salvia auriculata*	Petrucio and Estaves 2000
3	*Typha*	Beltman et al. 1990; Picard et al. 2005; Fraser et al. 2004
4	*Phragmites*	Yang et al. 2007; Beltman et al. 1990
5	*Glyceria*	Beltman et al. 1990
6	*Ulva rotundata*	Martinez et al. 2002
7	*Enteromorpha intestinalis*	Martinez et al. 2002
8	*Gracilaria gracillis*	Martinez et al. 2002
9	*Dicentrachus labrox*	Martinez et al. 2002
10	*Lemna*	Ansari and Khan 2008; Smith et al. 2004; Smith 2007; Tripathi and Upadhyay 2003; Jayaweera and Kasturiarachchi 2004
11	*Spirodela*	Ansari and Khan 2009b; El-Shafai et al. 2007
12	*Eichhornia crassipes*	Ansari and Khan 2011; Fox et al. 2008; Tripathi and Upadhyay 2003; Jayaweera and Kasturiarachchi 2004
13	*Pistia stratiotes*	Polomski et al. 2009; Lu et al. 2010
14	*Scirpus validus*	Polomski et al. 2009
15	*Phalaris arundinacea*	Polomski et al. 2009
16	*Thalia geniculata*	Polomski et al. 2008
17	*Oenenathe javanica*	Polomski et al. 2008
18	*Phyla lanceolata*	Polomski et al. 2008
19	*Scirpus validus*	Fraser et al. 2004; Picard et al. 2005
20	*Carex lacustris*	Fraser et al. 2004; Picard et al. 2005
21	*Phalaris arundinacea*	Fraser et al. 2004; Picard et al. 2005
22	*Pennisetumpurpureum*	Yang et al. 2007
23	*Polygonum hydropiperoides*	Martins et al. 2010
24	*Canna indica*	Yang et al. 2007
25	*Caladium*	Zul Hilmi et al. 2011
26	*Spinacia oleracea*	Zul Hilmi et al. 2011
27	*Zizania latifolia*	
28	*Sagittaria sagittifolia*	
29	*Ipomoea aquatica*	Li et al. 2009; Hu et al. 2008; Li et al. 2007
30	*Jasminum sambac*	Liu et al. 2004
31	*Cyperus alternifolius*	Liu et al. 2004
32	*Coleus blumei*	Liu et al. 2004
33	*Pandanus pygmaeus*	Joycel et al. 2010
34	*Azolla pinnata*	Tripathi and Upadhyay 2003; Jayaweera and Kasturiarachchi 2004
35	*Hibiscus cannabinus* L	Ikeda et al. 1999

Scirpus validus was found to be most effective while *Phalaris arundinacea* was generally least effective in reducing N in monocultures. Mixture of Four-species such as *Scirpus validus*, *Carex lacustris*, *Phalaris arundinacea,* and *Typha latifolia* was shown to be highly effective in the removal of the nutrients (Fraser et al. 2004).

17.5.4 Nutrients Loading

Various studies showed that the nutrients removal is directly related with increased nutrients concentration in the medium. The plant biomass positively correlated with nutrients supplied and therefore had higher depletion rate of nutrients (Polomski et al. 2009).

17.5.5 Temperature

Optimum growth was recorded at between 20 and 30 °C for *Lemna minor* and between 25 and 30 °C for *Spirodela polyrrhiza*. This temperature interval was found the most suitable for remediation of eutrophic water (Ansari and Khan 2008; Ansari and Khan 2009b). Experiments on warming mesocosms of shallow communities by 4 °C demonstrated changes in concentrations of soluble phosphate, total N and conductivity, increased total plant biomass and decreased algae

production owing to shading by floating plants (Feuchtmayr et al. 2009).

17.5.6 pH

It has been found that *Lemna minor* performs better at low pH for phytoremediation of eutrophic waters (Ansari and Khan 2008) and for increased treatment efficiencies in duckweed-covered wastewater, pH values should be decreased (Ansari and Khan 2009b; Ansari et al. 2011b).

17.5.7 Light

Recently, it has been shown that light is the significant factor controlling plant growth in a eutrophic lake (Karlsson et al. 2009). Various treatments of light showed a significant effect on photosynthesis and acclimation in aquatic macrophytes. It was found that in eutrophicated coastal waters seagrass decline is largely owing to low light intensity because of high biomass of algal overgrowth as epiphytes and macroalgae in shallow coastal areas, and phytoplankton in deeper coastal waters (Burkholder et al. 2007).

17.5.8 Seasonal Variations

In addition to more favorable temperatures during a particular season, there is some phenological specificity in developing plant biomass, which is contributing to higher plant growth during the season and therefore contributing to higher nutrients removal efficiency. Nutrient removal exhibited a typical seasonal pattern in microcosms with planted *Carexla custris*, *Scirpus validus*, *Phalarisa rundinacea,*and *Typha latifolia,* with higher removal rates in the growing season and lower rates in the winter months (Picard et al. 2005). During the autumn season, *Phragmites spp.* and *Typha latifolia* reached their optimum growth rate, followed by a dormant phase, which affected their nutrient removal efficiency (Kouki et al. 2009). Wetlands vegetated by *Pennisetum purpureum* significantly outperformed wetlands with other plants in May and June, whereas wetlands vegetated by *Phragmites communis* and *Canna indica* demonstrated higher removal efficiency from August to December (Yang et al. 2007).

17.6 Phytoremediation of Eutrophic Water Using Aquatic Macrophytes

The growth response of common duckweed *Lemna minor* was studied at various temperature and pH levels for its possible application for remediating eutrophic waters. The dry weight, chlorophyll *a*, nitrogen, phosphorus, potassium, peroxidase (POD), catalase (CAT), and malondialdehyde (MDA) levels were determined. While optimum growth was recorded at between 20 and 30 °C, reduced growth and an increase in protective enzymes were noted at both lower and higher temperatures. There was oxidative damage at temperatures less than 10 °C and greater than 40 °C. The pH of the growth medium was inversely related to the growth responses of *Lemna minor*. At acidic pH and at temperatures between 20 and 30 °C, the environmental conditions were most suitable for phytoremediation of eutrophic waters. Under these conditions, and when harvested regularly, *Lemna minor* was found to be useful in counteracting eutrophication (Ansari and Khan 2008). The range of pH from 6.5 to 6 and temperature of 25–30 °C were found to be the most suitable environmental condition for remediation of eutrophic water using giant duckweed. When harvested regularly duckweed plants were suggested to be useful in counteracting eutrophication in affected water bodies (Ansari and Khan 2009a).

Phytoremediation potential of duckweed *Lemna minor* L. was studied in vitro for the period of 7 days to investigate the removal of pollutants in domestic wastewater with special reference to nutrients. The study was conducted in plastic tubs of 6 inches deep and of 175 cm diameter. Twenty liter domestic wastewater was used in tubs for the culture of duckweed. The domestic wastewater quality was assessed by analyzing physicochemical characters and the resulting data were indicated as initial value. 1Hundred grams of fresh weight of *Lemna minor* L was cultured for the period of 7 days and again domestic wastewater was analyzed for the same physicochemical parameters and obtained values were indicated as final value. Net primary productivity (NPP) of duckweed was also determined by Harvest method for the period of culture. The study revealed that pH, dissolved oxygen and percentage oxygen saturation value had increased, while the values for other studied physico chemical parameters decreased significantly after seven days of culture of *Lemna minor* L. An increase in value of pH, dissolved oxygen, percentage oxygen saturation and decrease in value of alkalinity, carbon di oxide concentration, chloride, COD, hardness, nitrogen, and phosphorus value indicated an improvement in water quality. An increase in fresh weight of *Lemna minor* L. and NPP value have suggested its great potential in Phytoremediation for removal of pollutants with special reference to nutrients like nitrogen and phosphorus from domestic wastewater (Patel and Kanungo 2010).

The potential of *Eichhornia crassipes* was tested at various temperature and pH levels for its application for remediation of eutrophic water. The dry weight, chlorophyll-*a*, nitrogen, phosphorus, potassium, POD, CAT, and MDA levels were determined. Optimum growth of plant was recorded at pH levels 6 to 7 and between 20 and 30 °C temperatures. A significant reduction in growth and an increase in protective

enzymes were recorded above 35 °C temperature. The pH 6 to 7, temperature between 20 and 30 °C and replacing old plants with fresh plants were few conditions that were found to be most suitable for phytoremediation of eutrophic water using *Eichhornia crassipes* (Ansari and Khan 2011).

Water hyacinth has been used in aquatic systems for wastewater purification in the last few years. The role of water hyacinth (*Eichhornia crassipes*) species in polishing nitrate and phosphorus concentration from municipal wastewater treatment plant effluent by phytoremediation method has been evaluated. The objective of this project is to determine the removal efficiency of water hyacinth in polishing nitrate and phosphorus, as well as to calculate COD. Water hyacinth has been considered as the most efficient aquatic plant used in removing vast range of pollutants such as organic matters, nutrients, and heavy metals. Water hyacinth, which is also referred as macrophytes, was cultivated in the treatment house in a reactor tank of approximately 90(L) x 40(W) x 25(H) in dimension which is built with three compartments. Three water hyacinths are placed in each compartments and water sample in each compartment is collected in every 2 days. The plant observation was conducted by weight measurement, plant uptake and new young shoot development. Water hyacinth has been shown to remove approximately 49% of COD, 81% of ammonia, 67% of phosphorus, and 92% of nitrate. It has also showed significant growth rate at starting from day 6 with 0.33 shoot/day and they kept developing up to 0.38 shoot/day at the end of day 24. From the studies conducted, it has been proved that water hyacinth is capable of polishing the effluent of municipal wastewater which contains undesirable amount of nitrate and phosphorus concentration. (Kutty et al. 2009).

A study was conducted to remove the nutrients from the surface water of two golf courses by using the phytoremediation system. *Caladium sp.* and spinach (*Spinacia oleracea*) were used for the study. The results of this study may be used for new treatment of golf course surface water since this emerging technology is becoming significant toward green technology for national development (Zul Hilmi et al. 2011). Phytoremediation technology using aquatic plants in constructed wetlands and storm water detention ponds has been increasingly applied to remediate eutrophic waters. Effectiveness and potential of water lettuce (*Pistia stratiotes* L.) in removing nutrients including nitrogen (N) and phosphorus (P) from storm water has been evaluated in the constructed water detention systems before it is discharged into the St. Lucie Estuary, an important surface water system in Florida, using phytoremediation technologies. The results from this study indicate that water lettuce has a great potential in removing N and P from eutrophic storm waters and improving other water quality properties (Lu et al. 2010).

This study also indicates the potential utility of water hyacinth for nutrient removal and biomass production, based on the continuous harvest at the sustainable yield (MSY). Two types of surplus production–harvest models of water hyacinth are constructed to manage the water quality of rivers in both rainy and dry seasons. The models are expected to be a simple but adequate tool of pollution control for diffuse sources in the long term. The case study with Tha-chin River in Thailand shows that effective nutrient removal can be achieved under biomass control by harvesting at MSY. Nutrient removal in the rainy season is also investigated taking into account the quantity of biomass that flows in and out of the river basin (Mahujchariyawong and Ikeda 2001).

Two aquatic plants, *Zizani alatifolia* and *Sagittaria sagittifolia*, have been used to study the variation of physiological responses and the water qualities under mild, moderate, and weighty eutrophic water in plastic pot scale experiments. The physiological characteristics of both plants are investigated, which included contents of leaf MDA and proline, membrane permeability (MP), and activities of CAT and POD. The water qualities are analyzed correspondingly. The results showed remarkable effects of different degree of eutrophic water on physiological characteristics of the plants. These results suggested that *Zizania latifolia* and *Sagittaria sagittifolia* are the recommended aquatic plants in phytoremediation of mild and weighty eutrophicated water, respectively.

Phosphorus (P) fractions and the effect of phytoremediation on nitrogen and phosphorus removal from eutrophicated water and release from sediment have been investigated in the ecoremediation experiment enclosures installed in the Hua-jia-chi pond (Hangzhou city, Zhejiang province, China). The main P fraction in the sediment is inorganic phosphorus (IP). For the mesotrophic sediments, IP mainly consisted of HCl-extractable P (Ca-P). The annual average concentration of total nitrogen (TN), total phosphorus (TP) in water and the content of TN, TP in different vertical depth of sediment in the experiment enclosures with hydrophyte are always much lower than those in the control enclosure without hydrophyte and those outside of experiment enclosures. Therefore, it is suggested that phytoremediation was an effective technology for N and P removal from eutrophicated water and release from sediment (Xiang et al. 2009). *Ipomoea aquatica* with low-energy N^+ ion implantation has been used for the removal of both nitrogen and phosphorus from the eutrophic Chaohu Lake, China. The ion implantation is suggested to enhance the growth potential of *I. aquatica* in real eutrophic water and increase its nutrient removal efficiency. Thus, the low-energy ion implantation for aquatic plants could be considered as an approach for in situ phytoremediation and bioremediation of eutrophic waters (Li et al. 2009).

In a greenhouse study, *Cyperu salternifolius, Coleus blumei,* and *Jasminum sambac* have been cultured in a floating phytoremediation system with plantation cups inserted into a polyfoam plate that floated in the upper part of a tank filled

with 100 L domestic wastewater. The results showed that *Cyperus alternifolius* and *Coleus blumei* could grow well in the floating phytoremediation system while *Jasminum sambac* could not grow well, being 125.0% of the initial weight of planting. The removal rate of TN by these three plants was 68.0, 62.0, and 45.0% and that of NO3-N, COD, Cr and TP was 98.0, 80.0, and 92.0%, 78.0, 66.0, and 55.0%, and 90.6, 90.5, and 88.0%, respectively. *Cyperu salternifolius* and *Coleus blumei* have been shown to impose good effects on the removal of pollutants in the floating phytoremediation system (Liu et al. 2004).

Wetlands can be used in a cost-effective manner to treat nutrient-rich water for release nutrients from freshwater ecosystems using macrophyte, *Ipomoea aquatic* Forsskal (swamp cabbage), in a horizontal-flow, deep flow Technique (DFT) system. The removal of nutrients (total nitrogen and total phosphorus) varied between 41.5 and 75.5%. The results of this study indicate that cultivating edible, aquatic macrophytes with nutrient-rich, eutrophic water in a DFT system can be an effective, low-cost phytoremediation technology to treat water with undesirable levels of nitrogen and/or phosphorus (Hu et al. 2008).

The phytoremediation potential of water hyacinth, *Eichhornia crassipes* (Mart.) Solms, was examined in two independent studies. A modified Hoagland solution was added to ponds containing water hyacinths which were rated and measured for 4 weeks. The hyacinths accounted for 60–85% of the N removed from solution. Tissue N increased linearly with dry matter gain, but total nitrogen removal from the water increased exponentially with net dry matter gain or with an increase in canopy cover. The relation between total N in plant tissue and N removal from the water was similar for the two experiments (Fox et al. 2008).

There is a need to explore some "nonconventional" methods which are not only economically viable and easy to operate but ecofriendly as well. For remediation of village ponds, the first step is to remove the excess nutrients dumped in it. For this purpose, plant based bioremediation (phytoremediation) technology is the most promising option. Any aquatic plant that is capable of recovering or extracting nutrients or pollutants and has a fast growth rate coupled with high nutritive value is an excellent candidate for bioremediation of waste water. Such plants grow very fast utilizing waste water nutrients and also yield cost-effective protein rich plant biomass as a byproduct.

Duckweeds hold immense potential for both nutrient recovery and utilization as fodder or feed for livestock including fish. Wastewater-duckweed-aquaculture is a perfect ecofriendly integrated package for converting the waste water nutrients into high-quality fish protein and augmenting rural economy through generating employment opportunities and additional food security (Ansal et al. 2010).

The aim of this study was to investigate the use of water spinach (*Ipomoea aquatic* Forsk.) with N^+ ion-beam implantation for removal of nutrient species from eutrophic water. The mutated water spinach was grown on floating beds, and growth chambers were used to examine the growth of three cultivars of water spinach with ion implantation for 14 days in simulated eutrophic water at both high and low nitrogen levels. The specific weight growth rates of three cultivars of water spinach with ion implantation were significantly higher than the control, and their NO_3-N and NH_4-N removal efficiencies were also greater than those of the control. Furthermore, compared with the control, the nitrogen contents in the plant biomass with ion implantation were found to be higher (Li et al. 2007).

When *Pandanus pygmaeus*, a known hyperaccumulator, was planted in three of five setups with different treatments and different amounts of nitrates and phosphates have been given to allow, maximum algal growth, and are added to two of the setups containing the plants, and to other two without plants. Results showed that the plants could reduce algal growth, whereas the additional nutrients do not have significant adverse effects on plant growth. This proves that *P. pygmaeus* has a relatively high potential for removing nutrients, especially nitrates, thereby improving the quality of eutrophic waters and preventing algal blooms (Joycel et al. 2010).

The nutrient depuration capacity of *Polygonum hydropiperoides is measured* by cultivating plants in water obtained from fish ponds. The experiment simulated varying degrees of nutrient enhancement by using pond water enriched with nitrogen (N) and phosphorus (P). The sources of N and P were urea and diammonium phosphate, respectively. The best performance that has been recorded is a water depuration rate of 74% for N and 81% for P. These results suggest *Polygonum* as a good system to remove excess nutrients from aquaculture sites (Martins et al. 2010).

17.7 Discussion

Water eutrophication has become a worldwide environmental problem in the recent years. The development of novel technologies for controlling or remediating eutrophic water is drawing attention of many scientists and government organizations (Yang 2009). Recently, many major technologies have been developed for controlling or remediating water eutrophication which include: (1) external source pollution control, such as establishing sewage water treatment plants and abatement of agricultural nonpoint pollution; (2) internal-source pollution control, such as sediment removal, and immobilization of P; (3) water replacement and intensifying water flux; (4) biomanipulation approach using fish or aquatic animals to remove nutrients and control algal bloom;

(5) phytoremediation controlling both point and nonpoint sources of pollution (Yang 2009).

The change in the eutrophic conditions is reflected in the occurrence, pattern of distribution, and diversity of the biotic community (Ansari et al. 2011c). The limnological studies of lakes, rivers, and streams have been emphasized owing to deterioration of water quality because of eutrophication (Ansari et al. 2011b; Garg et al. 2002; Jha and Barat 2003). Nutrient removal capacity of some important aquatic plants such as *Eichhornia crassipes*, *Lemna minor,*and *Azolla pinnata* have been tested individually as well as in combinations in microcosms. Maximum removal was observed in species mixtures, involving *E. crassipes* and *L. minor* (79 % N) (Tripathi and Upadhyay 2003; Jayaweera and Kasturiarachchi 2004).

Various methods have been investigated for improving water quality specially the bioremediation of water using algal colony or other aquatic plants**.** Plants from the family Lemnaceae are widely used in ecological engineering projects to purify wastewater and eutrophic waterbodies (Fang et al. 2007). In phytoremediation plants can be used for pollutant stabilization, extraction, degradation, or volatilization (Smith et al. 2004). Phytoremediation by kenaf (*Hibiscus cannabinus* L.) was applied to improve eutrophic water quality. The growth of kenaf was satisfactorily achieved in water environment and nutrients were removed from eutrophic water body (Ikeda et al. 1999).

The excessive addition of nutrients to water causes quality problems and is one of the major causes of eutrophication in fresh water ecosystems (Ansari and Khan 2002, 2007, 2009a). The eutrophication process directly or indirectly affects the physical, chemical, and biological characteristics of an aquatic ecosystem (Ansari and Khan 2006a, b). The potential of various aquatic macrophytes for phytoremediation of various pollutants in water has been determined by various workers (Chaudhari 2002; Manu and Chaudhari 2002; Chandrashekhar et al. 2003). Phytoremediation, popularly known as green clean, is an emerging technology for the cleanup of contaminated sites by the use of plants, and is ecofriendly and low-cost technology compared with traditional engineering remediation methods (Diwan et al. 2008).

The environmental factors viz. nutrients, temperature, pH, dissolved oxygen, carbon-di-oxide, light, within a water source have major role in controlling eutrophication in aquatic bodies and limiting the growth and development of aquatic plants (Lau and Lane 2002; Shen 2002). The pH regulates the origin, mobility, and availability of ions and their different forms in water bodies (Huang et al. 2005). The uptake of nutrients by aquatic plants shows a direct relation with pH of the medium (Cordes et al. 2000). The range of light intensity influences the photosynthesis and acclimation of aquatic macrophytes. The aquatic macrophytes are reported to remove about 60–80 % nitrogen (Fox et al. 2008) and about 69 % of potassium from water (Zhou et al. 2007). Growth responses of aquatic plants **indicate eutrophic state of water (Smith** 2007). The effectiveness of aquatic plants was also evaluated for their capabilities in removing heavy metals from water (Skinner et al. 2007).

A lot of work has been done and a huge amount of capital has been invested for the restoration of some major and important water bodies that are besieged under the direct threat of eutrophication, but results are not very satisfactory. Beside the mechanical purification of water, biological methods such as phytoremediation technologies are required as they are very low-cost, most effective and sustainable measures to control water eutrophication. The research should be done to produce cost-effective phytoremediation systems using aquatic macrophytes for the recovery of nutrients from eutrophic waters. The role of various limiting factors (viz. best/worst performance of aquatic plants, nutrient concentrations, temperature, pH, light, seasonality) in developing a sustainable phytoremediation system should be identified. The harvested plant material (grown in phytoremediation system) can be utilized as livestock food, raw material, for biofuel production and toxicity testing of waters.

17.8 Future Perspectives

Ecological research should be done on important aspects like causes, consequences, and controls of water eutrophication. Studies should be conducted on phytoremediation including offsite nutrient removal by constructed wetlands to abate both point and nonpoint nutrient pollution and in situ phytoremediation using floating ecoislands system in suitable environmental conditions with enhanced nutrient removal capacity. Large treatment ponds can be developed and tested where limiting factors will be controlled by mechanically engineered and technological means to enhance the nutrients recovery from eutrophic waters. The work can further be extended to develop cost-effective methods of large-scale phytoremediation using aquatic macrophytes.

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Ultraviolet Radiation and Bromide as Limiting Factors in Eutrophication Processes in Semiarid Climate Zones

18

Elias Salameh, Sura Harahsheh and Arwa Tarawneh

Abstract

Eutrophication studies were conducted at four selected sites of surface water bodies in Jorden: viz. King Abdullal Canal in the Jordan Valley, Mujib dam, Wadi Rajil dam in the eastern desert of Jordan, and Muwaqqar dams in the eastern highlands of Jordan. The factors responsible for eutrophication processes are high NO3, PO4, and K concentrations in addition to sunlight, high temperature, and micronutrients, such as, Zn and Fe. When these dam reservoirs and canals were examined they were found to have all the suitable conditions but no eutrophication. Water reservoirs in the desert areas of Jordan seemed not to develop eutrophication owing to the high UV radiation lasting for about 330 days a year with average sunlight duration of 9.5 h a day. UV radiation was found to be the limiting factor in eutrophication processes. Other water bodies, especially in the Jordan Valley area contain high concentrations of bromide, of more than 500 µg/l. Bromide is a strong oxidant and seems to be responsible for the non-development of eutrophication processes, although all other factors which enhance eutrophication were available.

Keywords

Eutrophication · King Abdullah canal · Mujib dam · Wadi Rajil dam · Muwaqqar dams

18.1 Introduction

Eutrophication studies were conducted at four selected sites of surface water bodies in Jorden; viz. King Abdullal Canal in the Jordan Valley, Mujib dam, Wadi Rajil dam in the eastern desert of Jordan, and Muwaqqar dams in the eastern highlands of Jordan (Fig. 18.1). The four sites include three water storage facilities (dams and weirs) and an artificial water conveyor system, namely King Abdullah Canal. The climatic conditions in the four sites are generally arid to semiarid. In all four water bodies the prevailing conditions, such as, availability of macro- and micronutrients, solar illumination, relatively high water temperatures should result in water eutrophication, but eutrophication has not occurred in these water bodies.

The results of this study indicate that the conditions defined in the literature (Rook 1974, Carpenter et al. 1998, Zwiener 2006) as limiting factors for eutrophication processes are not the only factors preventing eutrophication from taking place. It seems that strong UV radiation in arid and semiarid climates with high solar illumination is a factor restricting eutrophication processes in these areas. Strong UV radiation during the day seems to restrict algae activities including algae multiplication. In such a case the algae hide under the water and remain inactive during the day when strong UV radiation affects the surface layers of a water body. It also seems that relatively high bromide concentrations in the surface water bodies in the Jordan Valley area limits algal activities.

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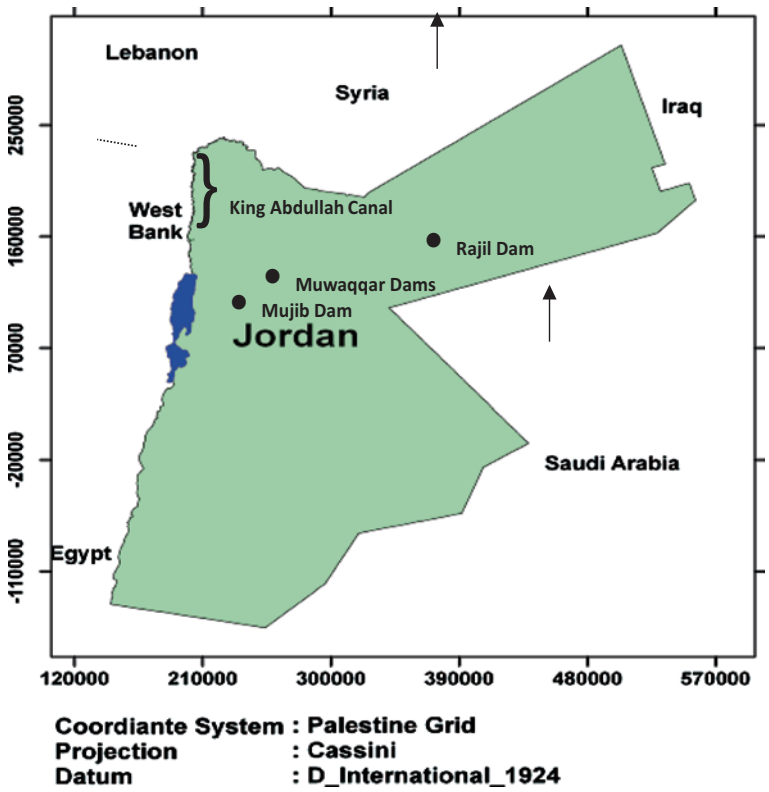

Fig. 18.1 Locations of study sites

18.2 Site 1: King Abdullah Canal (KAC)

The King Abdullah canal is a significant water project in the country, as it is a main municipal and agricultural water project for the Kingdom of Jordan. However, its water quality and quantity depend on the water supplied from outside sources in Israel and Syria. This canal extends from the upper part of the Jordan Valley at Adasyeh down to the Dead Sea with a total length of 110 km. The water originates from the Yarmouk River, the international Jordan border with Syria. The other sources are the Mukhaibeh Wells, the peace-conveyer water, from Israel, and along the canal the water from the side wadis and dams established on some of the side wadis such as the Wadi Al Arab and Ziglab, (Al-Khoury 2005; Hussein 2005; Ansari and Salameh 2006). Presently, 60–70 MCM/year of water are pumped from KAC to Amman with the provision for treatment at the Zai plant, located between Deir Alla, the water intake site and Amman (Jordan Valley Authority and Water Authority of Jordan, Open file).

18.2.1 The KAC Study Area

The present study area extends along the KAC from its intake at the Yarmouk to Deir Alla, at an elevation of 235 m below sea level to the south, along the left-hand side of the Jordan River terraces with a length of 65 km. The coordinates of the canal are 32° 10′ 3.53″ N to 32° 39′ 48.70″ N and 35° 34′ 49.70″ E to 35° 36′ 13.72″ E in Universal Transverse Mercator Grid (UTM) (Fig. 18.2).

The main objectives of this work were to study the parameters of the water which lead to algal activity, especially blue-green algae, phyto- and zoo-plankton, bacteria, and the eutrophication processes themselves. The parameters are: PO_4^{3-}, NO_3^-, light, temperature, and concentrations of trace metals which are generally available in urbanized catchments.

Water samples were collected monthly, along the KAC from the Yarmouk River at Nafq site to Deir Alla, from King Talal Dam KTD) and from mixtures of KAC with KTD water. Sampling site details are provided in Table 18.1 and Fig. 18.2.

18.2.2 Results

18.2.2.1 Nutrients

The highest concentrations of phosphate ions (PO_4^{3-}) were detected in the Yarmouk River while the lowest concentrations were found in the mixture of KAC and Ziglab Dam water (Fig. 18.3). Deir Alla and the mixture of KAC and Arab Dam waters have the highest concentrations of nitrate ions. The lowest nitrate concentrations were found in the

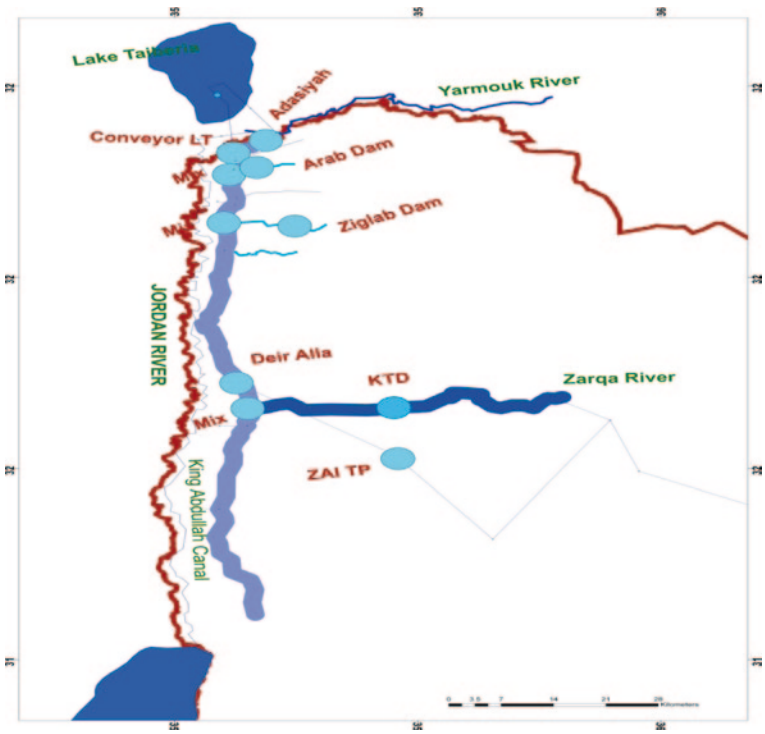

Fig. 18.2 The studied part of KAC and water carrier to Zai purification plant

Table 18.1 Sampling sites (Compare Fig. 18.2)

No	Site name
1	Yarmouk river (Nafq)
2	Mix (KAC + TibariasLake)
3	Mix (KAC + Arab Dam)
4	Mix (KAC + Ziglab)
5	DeirAlla
6	Mix (KAC + KTD)

Yarmouk River (Fig. 18.3). The average PO_4^{3-} and NO_3^- concentration in the winter months is higher than in summer months owing to the runoff flushing of the soils.

18.2.2.2 Biochemical Parameters

Biological oxygen demand (BOD_5), chemical oxygen demand (COD), total organic carbon (TOC), Chlorophyll-a, and Plankton Count were analyzed to study the presence of biological components in the waters of the study area.

18.2.2.3 COD

The COD values ranged from 1 mg/l in KAC (Deir Alla) in November 2005 to 50 mg/l in mixture of KAC and peace conveyor water during March 2006. The highest COD concentrations in these locations were found in the mixture of KAC and Arab Dam, Deir Alla, KTD during winter months. While in the summer months, the Yarmouk River, mixture of KAC and peace water, and Arab Dam showed the highest COD concentrations (Fig. 18.4).

18.2.2.4 BOD_5

The BOD_5 values ranged between 0 mg/l in specific locations to 39 mg/l in the mixtures of KAC and KTD water. The average BOD_5 values show higher concentrations in the summer months in all locations except in the mixture of KAC and KTD water in the winter months (Fig. 18.4).

18.2.2.5 TOC

The TOC values ranged from 0.92 mg/l in the Yarmouk River during March 2006 to 9.64 mg/l in mixture of KAC and KTD water during December 2005. The average TOC shows higher concentrations in the summer months except in the Yarmouk River, and in the mixture of KAC and peace waters which have higher concentrations in the winter months (Fig. 18.4).

From the above results, the mixtures of KAC and KTD have the higher concentrations of COD, BOD_5, and TOC followed by the mixture of KAC and Arab Dam water and KAC at Deir Alla.

18.2.2.6 Chlorophyll-a and Plankton Counts

Regarding the algae, all genera found in the last four locations (Yarmouk River, mixture of KAC and peace water and KAC at Deir Alla) were classified into six main groups (A–F) as illustrated in Table 18.2.

The concentrations of Chlorophyll-a and plankton counts were higher during the summer months than during the winter months in all the locations owing to high temperatures, nutrients, and light intensity, which encourage algal growth

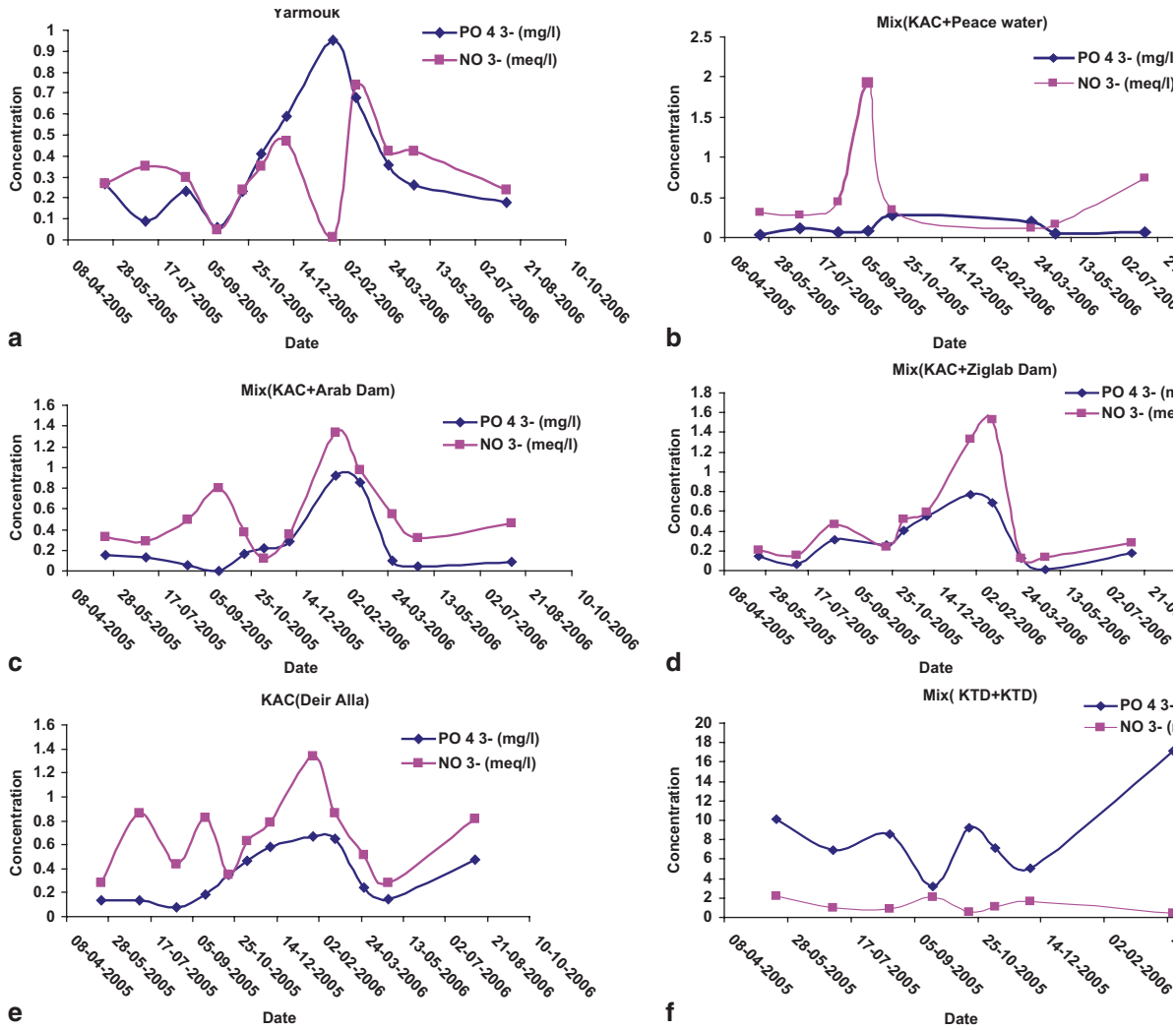

Fig. 18.3 The concentrations of PO_4^{3-} and NO_3^- for all sampled locations in the study area. **a** Yarmouk River, (PO_4^{3-}) and NO_3^- concentration. **b** Mixture of KAC and peace water, (PO_4^{3-}), and NO_3^- concentration. **c** Mixture of KAC and Arab Dam water, (PO_4^{3-}), and NO_3^- concentration. **d** Mixture of KAC and Ziglab Dam water, (PO_4^{3-}) and NO_3^- concentration. **e** KAC water at Deir Alla, (PO_4^{3-}) and NO_3^- concentration. **f** Mixture of KAC and KTD, (PO_4^{3-}), and NO_3^- concentration

in the canal water resulting in taste and odor problems. Phytoplankton play an important role in material and energy fluxes in eutrophic water systems (like in KAC) and they often control the DO and the nutrient budget as well as the pH values (Al-Harahsheh 2007).

During the day, algae consume CO_2 from the air by photosynthesis, which leads to decreases in the concentration of carbonic acid; consequently, the pH value increases, and O_2 concentration in the water also increases. On the other hand, during the night, the algal activity stops and the pH and DO values decrease. Thus differences in pH, DO, and temperature values between summer and winter can be used as a good indicator for the presence of algae in the canal water.

The highest concentration of Chlorophyll-a found in KAC at Deir Alla is followed by that of a mixture of KAC and peace water, while the mixture of KAC and peace waters showed higher plankton counts, followed by Deir Alla. Chlorophyll-a concentrations ranged from 1 ppb during January 2006 in the Yarmouk River water, to 23.3 ppb during March 2005 in the mixed KAC and peace waters, while the plankton count ranged from 5 unit/ml during April 2006 in the Yarmouk River to 2007 unit/ml in the same location during October 2005 (Table 18.3 and Fig. 18.5).

Of special importance in KAC water is the bromide concentration which ranges between 0.150 and 0.600 mg/l. This concentration is very high for a surface water body and may play the role of a controlling factor for eutrophication processes. UV radiation was measured in the Jordan Valley area along KAC indicating that it could be a controlling factor for algae activity, and hence eutrophication processes (Table 18.4).

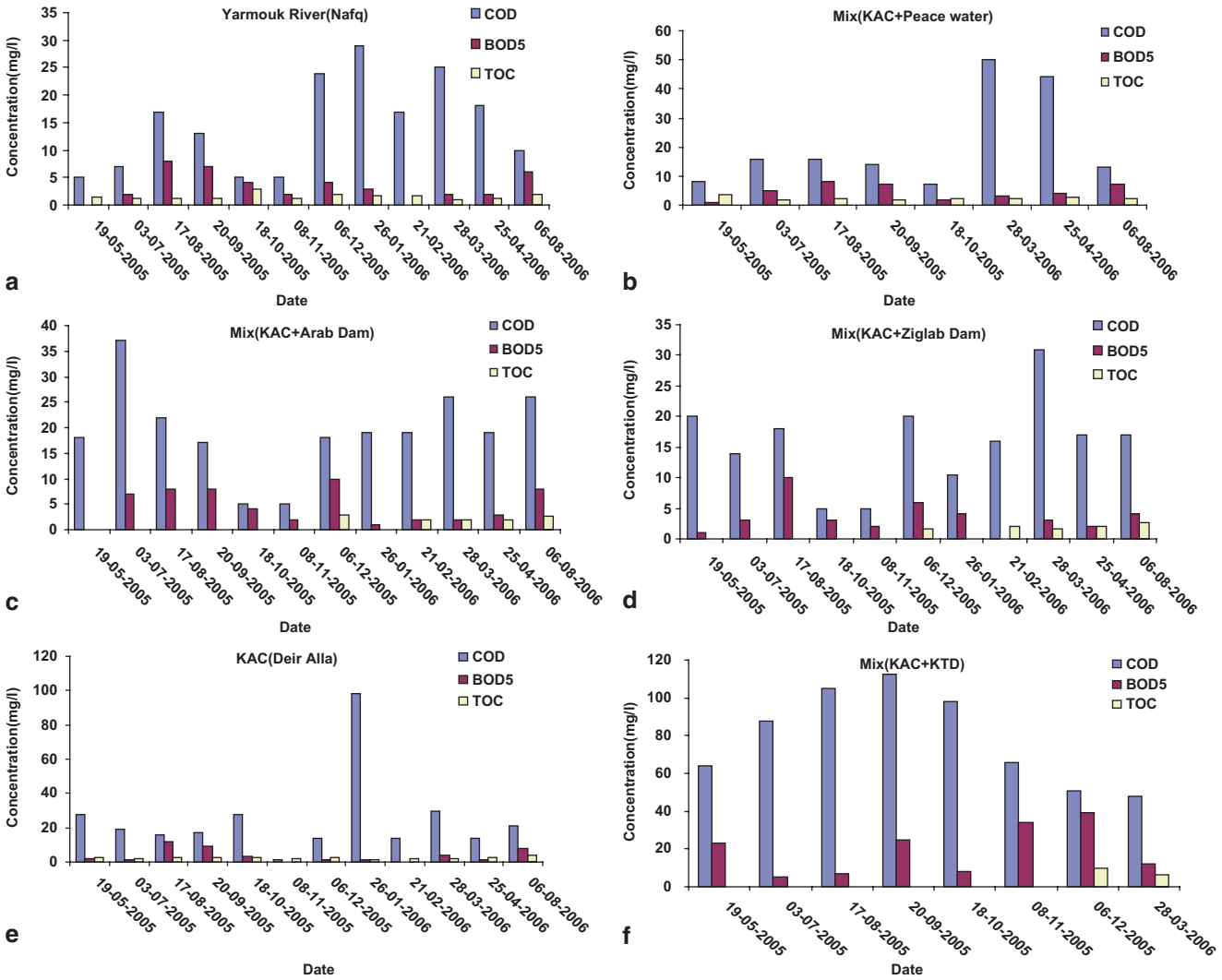

Fig. 18.4 Concentrations of COD, BOD_5, and TOC in the sampled locations of the study area. **a** Yarmouk River. **b** Mixture of KAC and Peace water. **c** Mixture of KAC and Arab Dam water. **d** Mixture of KAC and Ziglab Dam water **e** KAC water at Deir Alla. **f** Mixture of KAC and KTD water

18.3 Site 2- Mujib dam

Jordan built many dams to store flood and base flow water along the main rivers and wadis. All these dams receive every year, flood, and base flow water originating from their catchments, which are partly urbanized, containing light industries or are used in agricultural production.

18.3.1 Mujib Dam Study Area

Wadi Mujib is located between latitudes [95393–137739] N, and longitudes [205442–244775] E. The dam collects flood and base flow water (Fig. 18.6).

Land use and land cover of the Mujib catchment area strongly influence the chemistry of the dam's lake water and its temporal variations. The major land characteristics of the catchment area are: Sparse population, cultivated land and livestock, gypsum mines, disposal of wastewater in cesspits and fishing in the lake (Margane et al. 2008; Al-Harahsheh and Al-Amoush 2011; Harahsheh and Salameh 2011). To meet the aims of this study, the chemical parameters in Mujib dam water, which could lead to eutrophication processes, such as, PO_4^{3-}, NO_3^-, and SiO_2, in addition to the biological water constituents, such as, BOD5, COD, TOC, Chlorophyll a, plankton counts, were studied.

18.3.2 Results

The concentrations of the different parameters are affected by the different water sources feeding the dam; large variations in water flows, water velocity, human activity, and the

Table 18.2 Algal genus found in the main water sources of KAC

Yarmouk River		Mixture of KAC and peace water		DeirAlla	
Euglena	E	*Diatoms*	B	*Navicula*	B
Chlamydomonas	C	*Gomphonema*	F	*Chlamydomonas*	C
Coleochaete		*Trachelomonas*	B	*Zygnema*	E
Oikomoas		*Oikonomas*		*Oikomonas*	
Navicula	B	*Staurastrum*	A	*Dinomonas*	
Pinnularia	D	*Cladophora*	F	*Pinnularia*	D
Oedogonium	F	*Tetraedon*	C	*Cocconeis*	D
Dinomonas		*Euglena*	E	*Pelomyxa*	
Anisonema		*Gomphnema*	C	*Anisonema*	
Pelomyxa		*Senedsmus*	E	*Heliozoans*	
Cyclotella	B	*Spirogyra*	B	*Navicula*	B
Gomphonema	F	*Volvox*	A	*Cyclotella*	B
Scenedsmus	E	*Phacus*	C, E	*Scenedesmus*	E
Tetracystis				*Coelastrum*	E
Chlorococum	C			*Pediastrum*	E
Achly(funji)				*Cosmarium*	
Ceratium	A			*Chorella*	B
Gomphonema	C			*Schizochlamysm*	
Chlorococcus				*Stylosphaeridium*	
Oscillatoria	B, C*			*Chlorococcus*	
Diatoms	B			*Tetraedon*	C
Nitzschria				*Asterococcus*	
Micrasterias	D			*Tetraspora*	F
Clorella	B			*Euglena*	E
Spirogyra	B, C			*Spirogyra*	B, C
Cladophora	D, F			*Doctylococcopsis*	
Codium				*Aphanocapsa*	
Vaucheria	F			*Micasterias*	D
Tetraedon	C			*Gleocystis*	
Chaetophora	F			*Anisomonas*	
Gymodium				*Dionomonas*	
Staurastrum	A			*Chaetophora*	F
Crucigenia					

**Oscillatoria* is a blue-green characteristic alga for eutrophic water body (Ryding and Rast 1989).
A Taste and odor algae, *B* Filter clogging algae, *C* Polluted water algae, *D* Clean water algae, *E* Plankton and other surface water algae, *F* Algae growing on reservoir wells

Table 18.3 Concentrations of chlorophyll-a and plankton count in the test sites

Date	Yarmouk River		KAC + Peace water		KAC (DeirAlla)	
	Chlorophyll-a (ppb)	Plankton Count (Unit/ml)	Chlorophyll-a (ppb)	Plankton Count (Unit/ml)	Chlorophyll-a (ppb)	Plankton Count (Unit/ml)
19/05/2005	6.69	11	23.27	649	19.26	694
08/06/2005	5.55	17	16.24	160	16.67	67
03/07/2005	1.84	53	7.49	1275	10.83	1169
17/08/2005	5.42	28	10.54	1257	15.24	203
20/09/2005	13.5	718	8.33	1397	5.64	45
18/10/2005	11.85	2007	10.93	1023	11.08	1347
08/11/2005	2.47	14	9.94	762	4.11	63
06/12/2005	2.12	52			6.18	17
26/01/2006	1.00	14			1.51	44
21/02/2006	2.66	8			17.70	49
28/03/2006	2.04	6	8.40	8.16	17.30	19
25/04/2006	3.11	5	12.41	145	8.22	53

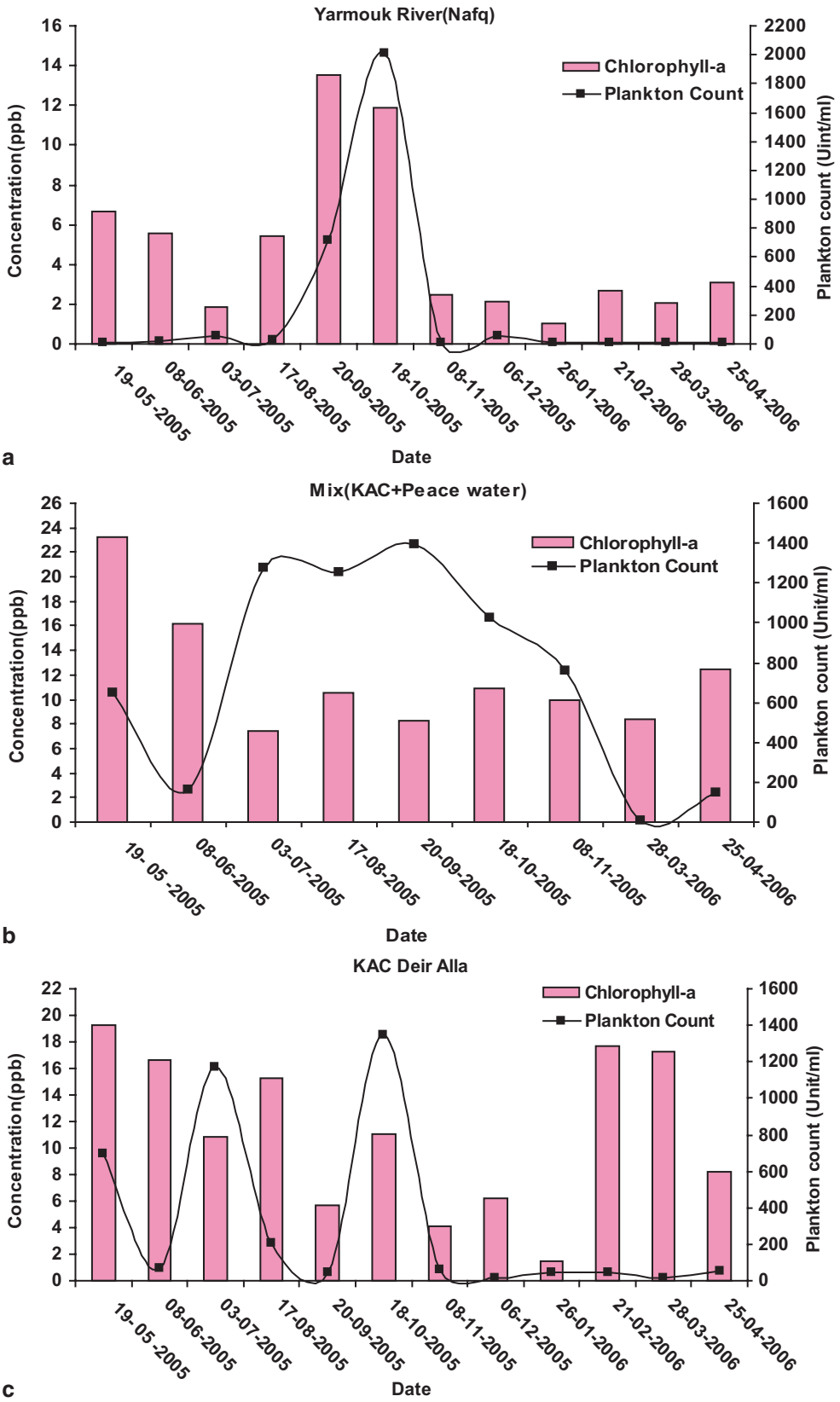

Fig. 18.5 The concentrations of Chlorophyll-a and Plankton Counts in the study area. **a** Yarmouk River. **b** Mixture of KAC and Peace water. **c** KAC water at Deir Alla

Table 18.4 UV radiation in Deir Alla areas (midday)

Radiation	Wave length (nm)	Intensity (mv/cm^2)
UV a	(315–400)	361
UV b	(280–315)	1.36
UV c	(200–280)	0.00

climatic variations occur between the winters and summer seasons. The seasonal average of some chemical laboratory analyses of water samples are given in Figs. 18.7 and 18.8.

18.3.2.1 Nutrients (PO_4^{3-}, NO_3^-, SiO_2)

The PO_4^{3-}, NO_3^-, and SiO_2 concentrations ranged between 0.01, 0.94, and 0.356 mg/l to 0.177, 3.98, and 15.55 mg/l, respectively. In general, the average concentrations of PO_4^{3-}, NO_3^- , and SiO_2 are higher in winter than in summer, except for the year 2006 when there was flushing of the soil by the runoff (Fig. 18.7). The concentrations of all the nutrients are above the eutrophication level. The NO_3^- and PO_4^{3-} concentrations necessary for the eutrophication process (Fig. 18.7) are 0.2–0.3 and 0.01 mg/l, respectively (Lee and Lee 2005). The main sources of nutrients are natural PO_4^{3-} originating from the phosphate deposits within the catchment area, natural NO_3^- from soils and the atmosphere and disposal of wastewater in cesspits, chicken farms, and cultivated lands inside the Mujib dam catchment area. The higher silica concentrations could be attributed to the dissolution of sandstone of Kurnub Formation or clay deposits in the study area.

18.3.2.2 Biochemical Parameters

BOD_5, COD, TOC, and Chlorophyll a, plankton counts were analyzed in the Mujib dam water.

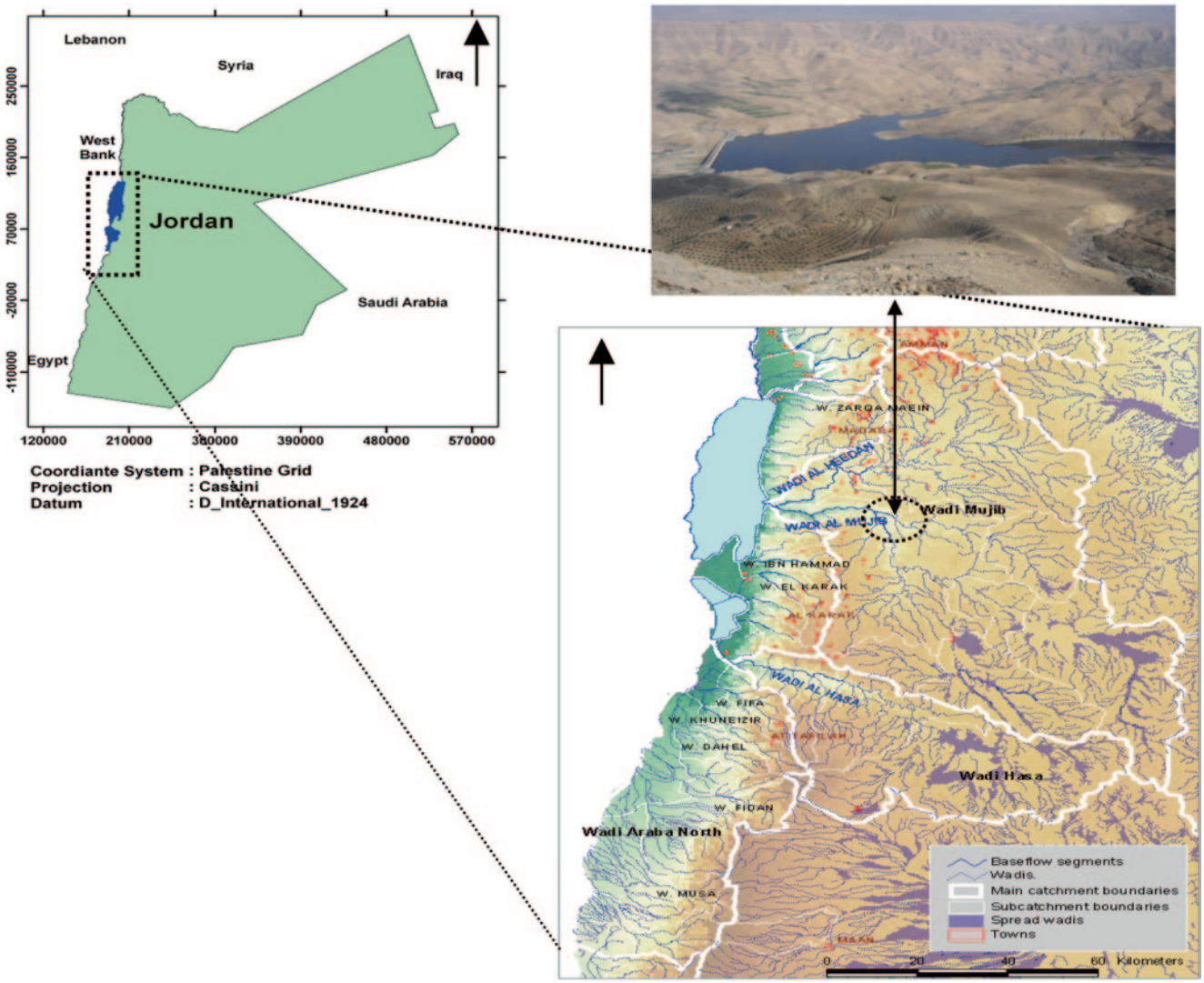

Fig. 18.6 Location map of Mujib dam (Photo) and its catchments area

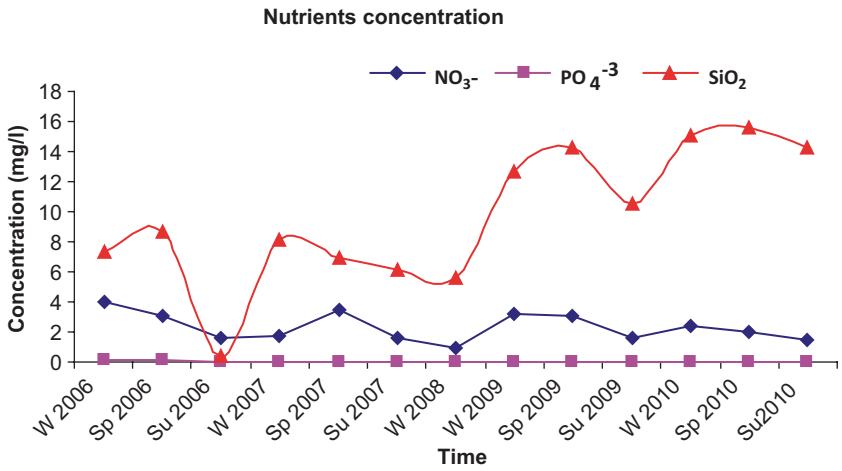

Fig. 18.7 Temporal variations of the average nutrients concentration of the Mujib dam water

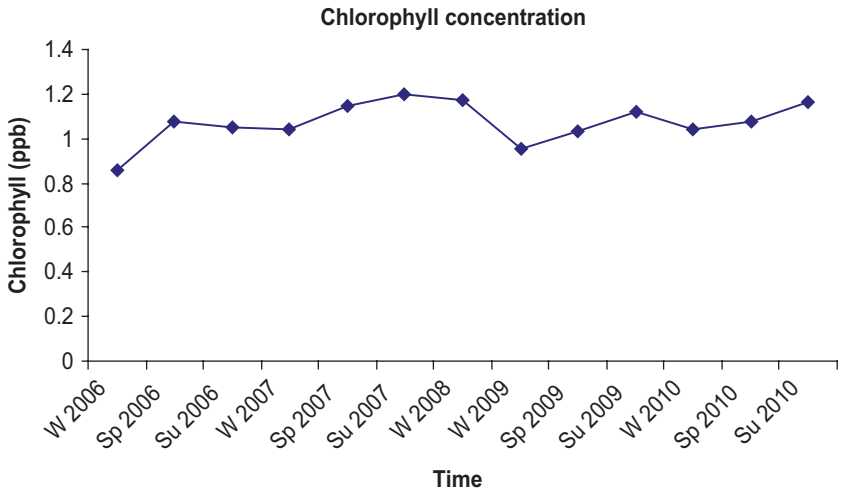

Fig. 18.8 Temporal variations of the average chlorophyll "a" concentration of the Mujib dam water

18.3.2.3 BOD_5

The BOD_5 concentrations in all samples for 2006, 2007, 2008, 2009, and 2010 were less than 10 mg/l.

18.3.2.4 COD

The COD concentrations in all seasons were less than 20 mg/l except in the winter 2007 and winter 2008 when values were more than 20 mg/l, but less than 30 mg/l.

18.3.2.5 TOC

The TOC concentrations in all samples were less than 2 mg/l.

18.3.2.6 Chlorophyll a and Plankton Count

The chlorophyll a concentrations showed small variations between summer and winter seasons; the average values ranged between 0.86 ppb in winter 2006 to 1.24 ppb in summer 2007. The chlorophyll a concentrations were found to be higher in summer than in winter owing to higher temperatures, nutrient availability, and high light intensity. However, in general the concentrations of chlorophyll a were very low in Mujib dam water compared with other dams in Jordan (e.g., Wadi Al Arab, King Talal Dam and King Abduallah Canal (KAC))(Al-Harahsheh 2007) (Fig. 18.8).

Table 18.5 shows the plankton count analyses in all samples from winter 2006 to summer 2010. The plankton counts in summer were higher than in winter. Plankton was not observed in winter time except in the winter of 2008 and 2009. The summer plankton counts ranged from 4 unit/ml in the summer of 2006 to 14 unit/ml in the summer of 2010. The plankton counts were found to be very low indicating that the algal concentrations are very small and the occurrence of eutrophication blooms is limited in the Mujib dam.

18.4 Site 3: Wadi Rajil Dam

18.4.1 General Information

Wadi Rajil is one of the streams feeding the Azraq Oasis; its catchment extends into basalt covered Syrian territories,

Table 18.5 Average plankton count in Mujib dam water

Time	Plankton count (unit/ml)
W2006	Not seen
S2006	4
W2007	Not seen
S2007	6
W2008	10
W2009	Not seen
S2009	11
W2010	5
S2010	14

the Jabal Druz area. The upper wadi course is oriented in a south easterly direction, gradually turning south westerly, and then westerly to discharge into the Azraq Oasis. The wadi is intermittent, discharging flood and snow melt water. Rajil dam was constructed on the wadi in the 1990s to collect the flood waters with the purpose of providing cattle watering and artificial groundwater recharge (Ass'ad and Abdualla 2010)

18.4.2 Climate

The climate of the dam surroundings is characterized by hot dry summers and moderately wet cool winters and can be classified as arid. The upper reaches of the catchment (Jabel Drouz area) enjoy a Mediterranean climate where rainfall averages 450 mm/yr decreasing exponentially to 80 mm/yr in the Rajil dam and Azraq area.

The potential evaporation rate in the dam surroundings is 2100 mm/yr, and the average relative humidity ranges from 52 to 62% during summer and from 70 to 80% during winter. The mean annual temperature is 19 °C. August is the hottest month with a monthly daily average temperature of 28 °C. January is the coldest month with a monthly daily average of 5 °C. Winds are moderate, easterly in summer and westerly in winter. The mean annual sunshine duration per day was 9 h in winter which was increased to 12 h in summer.

18.4.3 Runoff

Like all other wadis in the Azraq basin, Wadi Rajil is not gauged. The wadi bottom slope decreases from Jabal Drouz with a slope of 15 to 5–15% along the middle wadi reaches and to 3–5% along the lower reaches. Evaluating the runoff/precipitation ratio for the type of climate, landuse, topography, and geological conditions results in a ratio of 1.2% and in an average annual flood flow discharge of 3.85%.

Table 18.6 Chemical and physical parameters of Rajil reservoir water

Parameter	Floodwater	Reservoir water
TDS mg/l	346	749
pH	7.9	8.26
T °C	25	27
Ca mg/l	30.0	61.0
Mg mg/l	21.1	42.2
Na mg/l	36.4	72.9
K mg/l	7.23	14.5
Cl mg/l	23.1	46.9
SO4 mg/l	104	210
HCO3 mg/l	143	286
PO4 mg/l	0.020	0.051
NO3 mg/l	10.8	17.5
Fe mg/l	<0.02	0.09
Mn mg/l	<0.02	0.012

Table 18.7 UV radiation in Muwaqqar and Rajil areas (midday)

Radiation	Wave length (nm)	Intensity (mv/cm²)
UV a	(315–400)	415
UV b	(280–315)	1.52
UV c	(200–280)	0.00

18.4.4 Rock Types

The dam site and surroundings are covered by basalts underlain by chalky limestone with some chert beds of the Muwaqqar Tertiary Formation. Parts of the reservoir lake are covered by alluvial deposits of basalt, gravel, sand, silt, and clay.

18.4.5 Chemistry of the Dam Water

Within the Rajil dam catchment area, land use is restricted to some cattle grazing spread over the catchment area. The wastes of the sporadic human activities and those of grazing cattle are flushed by floodwater into the dam reservoir as dissolved and suspended loads contributing the necessary nutrients for the eutrophication processes of the reservoir water (Table 18.6). In addition, the climatic parameters in the area indicate all necessary conditions for eutrophication processes to take place are present, but eutrophication in that reservoir has not been observed, even after years of construction and water collection. It seems that the very high UV radiation of both the long wave and the intermediate wave UV do not allow algae to multiply and hence no eutrophication processes have occurred in the Rajil reservoir (Table 18.7).

18.5 Site 4: Muwaqqar Dams

In other desert dams, such as, the Muwaqqar dam reservoirs 1, 2, and 3, with similar nutrient concentrations to those prevailing in the Rajil reservoir and even with higher PO_4

Table 18.8 Chemical and physical parameters of the three dams water in Muwaqqar area

	Dam (1)	Dam (2)	Dam (3)
TDS (mg/l)	167	170	170
pH	8.05	8.11	8.2
TC^0	18.0	17.9	17.9
Ca (mg/l)	27.4	25.7	26.2
Mg (mg/l)	9.4	5.88	6.4
Na (mg/l)	22.05	17.0	15.0
K (mg/l)	4.8	4.8	4.3
Cl (mg/l)	10.5	11.1	10.7
SO4 (mg/l)	15.2	16.8	15.36
HCO3 (mg/l)	115.9	117.8	0.55
PO4 (mg/l)	0.511	0.63	16.4
NO3 (mg/l)	15.0	16.2	16.4
Fe (mg/l) average for the three dams		0.60–1.12	
Mn (mg/l) average for the three dams		0.03–0.05	
Zn (mg/l) average for the three dams		0.002	

and NO_3 concentrations of 0.5 and 15 mg/l, respectively, eutrophication has not taken place (Table 18.8). Other surface water bodies in the desert areas of Jordan, such as pools, close to both Wadi Rajil dam and the Muwaqqar dams which are used by farmers to temporarily store water for cattle watering or irrigation also do not develop eutrophication, although all known conditions leading to eutrophication processes including the limiting factors—minimum PO_4 and NO_3 concentration—are fulfilled (NWMP 2004).

The basalt cover of the area contains micronutrients such as a zinc, manganese, iron, and potassium. The UV measurements show very high radiation values starting from early morning to late afternoon.

18.6 Conclusions

In all four studied sites, the factors leading to eutrophication according to worldwide published work, such as, high nutrient concentrations, high solar illumination, suitable pH, high temperature, and the low water velocity) are conducive to causing eutrophication processes. In addition, all these conditions provide an ideal environment for many different algal species to grow and increase in numbers forming algal blooms. Nevertheless, the occurrence of eutrophication blooms is limited in King Abdullah Canal, Mujib Rajil, and Muwaqqar dams. One possible explanation for this finding may be the high UV radiation which may restrict eutrophication processes. In addition, the waters of the Jordan Valley area, including the sources of King Abdullah Canal water, contain high bromide concentrations, which also may restrict algal growth and hence also the eutrophication processes.

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